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THE ELECTRICAL CONDUCTIVITY OF VERY DILUTE HYDROCHLORIC AND NITRIC ACID SOLUTIONS.

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I. Purpose of the Investigation.

IT is well known that there is great difficulty in obtaining an exact value for the equivalent conductivity of completely dissociated acids, owing to the large effect of the impurities of the water on the conductivity of even strong acids in very dilute solutions. These give rise to a maximum value of the conductivity at a dilution of from 500 to 2,000 liters, and to a marked decrease in its value at greater dilutions. Yet a knowledge of the theoretical limiting value is of great importance, since upon it is based the assumed value of the equivalent conductivity of the hydrogen ion and the calculated degrees of dissociation of acids in general.

Kohlrausch[1] in 1898 derived values for the conductivity of strong acids at extreme dilution by adding to the observed value at 0.001 normal a quantity equal to the product of the observed increase

[1] Wied. Ann., **66**, 794 (1898).

between 0.001 and 0.00001 normal in the case of neutral salts by the ratio of the increase between 0.1 and 0.001 normal in the case of the acids to the corresponding increase in the case of neutral salts, the conductivity of the water having been first subtracted in all cases. By subtracting from these values the conductivity of the negative ions, which had been derived from the conductivity and transference values of neutral diionic salts, he arrived at the value 318 for the equivalent conductivity of the hydrogen ion at 18° C. — a value, however, which he regards only as a rough estimate. Three years later[1] he deduced also the temperature change of this conductivity, expressing it by the equation:

$$\Lambda_t = 318[1 + 0.0154(t - 18) - 0.000033(t - 18)^2].$$

Quite recently Noyes and Sammet[2] have deduced the equivalent conductivity of the hydrogen ion by an independent method; namely, by combination of the transference number of moderately dilute hydrochloric acid with the equivalent conductivity of the chlorine ion derived from transference determinations and conductivity measurements of potassium chloride. The value thus obtained is 330 at 18° or 3.8 per cent. greater than that of Kohlrausch. The authors consider that this divergence cannot be due to experimental errors, but that it must arise either from an error in the extrapolated values of the conductivity of acids at extreme dilution, or from some real defect in the theoretical considerations from which the identity of the results of the two methods is predicted.

As it seemed possible to eliminate to a great extent the effect of the impurities in the water by appropriate measurements of the conductivity of dilute acids and a treatment of the data by certain methods to be described below, we undertook an investigation in this direction, both with nitric and with hydrochloric acid, and desire now to present the results which have been obtained. It may be stated in advance that these results are in substantial agreement with the extrapolated value of Kohlrausch.

[1] Sitzungsberichte der Preuss. Akad. d. Wissenschaften, 1901, 1026.

[2] Journ. Amer. Chem. Soc., **24**, 965, 1902; **25**, 165, 1903. Zeitschr. phys. Chem., **43**, 49, 1903.

II. Preparation of the Solutions.

In the preparation of the solutions, water was used which had a specific conductance of $0.8 - 1.5 \times 10^{-6}$ reciprocal ohms and which had been purified by redistillation of ordinary distilled water to which alkaline permanganate was added, the first and last portions of the distillate being rejected. The acid solutions were made by adding to definite portions of this water weighed portions of a standard acid of strength about 0.01 normal. The standard hydrochloric acid solution was obtained by absorbing in water hydrogen chloride gas made from twice-precipitated sodium chloride and pure sulphuric acid. Its strength was determined gravimetrically by precipitating with silver nitrate and weighing the silver chloride in Gooch crucibles. The several determinations made showed an average deviation from the mean value of less than 0.05 per cent. A standard nitric acid solution approximately 0.01 normal was made by diluting chemically pure acid through which air had been drawn to remove any lower oxides of nitrogen dissolved in it. This was standardized against barium hydroxide solution, whose strength had been determined by two independent methods. Five 0.01 normal solutions of potassium chloride were used to obtain the cell-constant; these were made from a sample of the salt which had been twice precipitated with pure hydrochloric acid and then crystallized from water, dried, and ignited to incipient fusion. A 0.01 normal sodium chloride solution made from salt prepared in the same way was used as a check.

In all cases, for the sake of greater convenience and accuracy, the content of the solution was determined by weighing, and not by volume measurement; but the values thus obtained of the number of milli-equivalents of solute in 1,000 grams of water were invariably (both in the calculation of the cell-constant and of the specific and equivalent conductivity of the acid solutions) considered to be numerically identical with the concentration in milli-equivalents per liter of solution. That no appreciable error (not even one as great as 0.05 per cent.) is introduced by this assumption will be readily seen, since none of the solutions were stronger than 0.01 normal.

III. THE CONDUCTIVITY APPARATUS AND METHOD OF MEASUREMENT.

The conductance of the solutions was measured by the Wheatstone slide-wire bridge arrangement in the form recommended by Kohlrausch, using an alternating current produced by an induction coil, and a telephone as an indicator of zero potential. The bridge consisted of a marble drum on which was wound five meters of manganine wire. Five or six settings were made for each solution, so as to eliminate as far as possible any personal error in determining the exact point corresponding to the minimum sound in the telephone. The average deviation of the separate values from the mean was less than 0.1 per cent. except in the case of the extreme dilutions, where it amounted in a few cases to 0.3 per cent. The probable error of the mean was always less than 0.1 per cent.except in the case of water. Both the slide-wire and the rheostat used were carefully calibrated, and the corrections were found in no case to exceed 0.1 per cent. The resistance vessel for holding the solution whose conductance was to be measured was a platinum cylinder 15 cm. high and 5 cm. in diameter. Into this was inserted, so as to rest on the bottom of the cylinder, an inverted glass bell 4.4 cm. in diameter attached to a glass tube sealed near the bottom, as shown in Fig. 1.

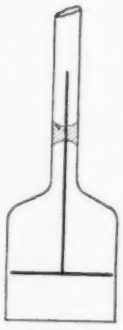

Fig. 1.

Into the bell an unplatinized but mechanically roughened platinum disk was sealed by means of a stiff platinum wire. The electrode was not platinized, so as to reduce as far as possible adsorption effects. It had an area of 15 sq. cm., and the distance between its lower surface and the bottom of the platinum cylinder was 1.9 cm. There was enough space along the side of this disk to allow the liquid to pass, and near the top of the bell a large hole was blown so that raising and lowering the glass plunger gave an efficient means of stirring. It was proved that the "cell constant" of the apparatus varied less than 0.05 per cent. with different settings of the plunger in the vessel. The use of a platinum vessel made it possible to collect the water at a little below the boiling temperature as it came off fresh from the still, whereby better water could be

obtained, as there was less chance for the absorption of carbon dioxide. The plunger passed through a vulcanite cap which fitted the top of the cylinder, and thus kept the solution from much contact with the air. The cylinder was immersed almost to the top in a thermostat kept always within 0.02° of 18°. The temperature was measured by a thermometer that had been standarized and corrected to the scale of an air thermometer. The room was also kept nearly at the same temperature to prevent condensation at the top of the cell. Contacts were made by mercury.

The solutions were made by adding successively a number of portions of standard acid (approximately 0.01 normal) from a weighed Beckman pipette to a weighed quantity (about 180 grams) of water in the vessel. The weight of the added portion could easily be determined to less than 0.5 milligram, or 0.05 per cent. in the case of the smallest portion. In this way a series of solutions, usually varying in concentration from about 0.0001 normal up to 0.001 or 0.002 normal, were prepared, and their conductance measured.

Several experiments were made to determine whether the conductivity of dilute acid solutions changed with time upon standing in the covered conductivity vessel in the thermostat. The change upon standing over night amounted to only 0.1 per cent. of the conductivity of a 0.0002 normal solution.

In order to confirm the accuracy of the method, similar series of measurements were made with potassium chloride solutions at the same dilutions as in the case of the acids. The results, which are communicated in the Section V., agree within 0.1 per cent. with those obtained by Kohlrausch and Maltby,[1] in their very accurate determinations published in 1900.

IV. Methods of Correcting for Impurities in Water at Great Dilution.

We have employed two methods for eliminating the influence of the impurities in the water on the conductivity of the acid solutions. Both of these involve the principle that *the total effect of the acid and of the impurities in the water on the conductivity of each other is*

[1] Wissensch. Abhandlungen d. phys.-technischen Reichsanstalt, **3**, 157–227, 1900. Zeitschr. phys. Chem., **36**, 750, 1901.

already produced when a relatively small quantity of acid has been added to the water, after which further additions of acid remain unaffected by the impurities.

In the first method of computation this principle is applied in a direct manner by simply subtracting the conductivity of a very dilute acid solution from that of a more concentrated one, and regarding the ratio of this difference to the difference in the respective concentrations as the equivalent conductivity of the acid at the higher concentration; that is, if $\varkappa_1$ and $\varkappa_2$ are the conductivities at the concentrations C_1 and C_2 respectively, C_1 being a very small concentration, it is assumed that

$$\frac{\varkappa_2 - \varkappa_1}{C_2 - C_1} = \Lambda_{c_2},$$

the equivalent conductivity at the concentration C_2.[1] Thus, the underlying idea is the preparation, by the addition of a little acid, of a sample of solvent the impurities in which shall have no appreciable influence on the conductivity of subsequently added portions of acid. Theoretically, it seems highly probable that this must be practicable; for any basic constituents of the water like ammonium or other alkaline hydroxides or carbonates would be completely neutralized, and any weakly acid constituent like carbonic acid which Kohlrausch[2] has shown to be undoubtedly the chief source of impurity, would have its dissociation reduced nearly to zero, as soon as the concentration of the strong acid added reached a value as great as, or a few times greater than, the concentration of the impurity. It is true that even though the impurities may have been thus rendered harmless, the increase in conductivity produced by

[1] In the calculation of Λ_{c_2} it is necessary to apply a slight correction to the observed conductance ($\varkappa_1'$), since when the second portion of acid is added the volume of the solution is somewhat increased, whereby the observed conductance and concentration would be decreased in the same proportion. Thus if m_w, m_1 and m_2 are the weights of water, of the first portion of added acid of a concentration C_0, and of the second portion respectively, then, placing volumes proportional to weights, which at the dilutions in question produces no error, we have:

$$\varkappa_1 = \varkappa'_1 \frac{m_w + m_1}{m_w + m_1 + m_2}.$$

Also

$$C_2 - C_1 = \frac{C_0 m_2}{m_w + m_1 + m_2}.$$

[2] Wissensch. Abhandlungen d. phys. tech. Reichsanstalt, **3**, 193 (1900).

the added portion of acid will not be strictly identical with the conductivity which it would have if it were added to pure water; for the acid originally present will be somewhat reduced in dissociation, and will itself reduce the dissociation of the added acid: but this effect is known to be very small at high dilutions, and the last-mentioned part of it is eliminated by regarding the calculated equivalent conductivity as corresponding to the final concentration rather than to the difference in concentration. [1]

In regard to the choice of the initial concentration, it may be pointed out that this must be taken so large that the maximum effect of the impurities in the water and of the acid on the conductivity of each other shall be attained, and that this condition is shown to be fulfilled when the equivalent conductivities calculated from two successive values of the initial concentration are in substantial agreement. The fact that such an agreement is actually found to exist even with relatively small values of the initial concentration is evidence of the correctness of the principle on which the computation is based.

The second method of computation is based on the assumption that the true values of the equivalent conductivity increase regularly to a maximum at the highest dilution, and that the decrease in the observed values from the maximum obtained at a moderate dilution is due to a *constant* error in the specific conductance arising from the effect of the impurities in the water. Therefore it is justifiable to add to the observed values of the specific conductance such a quantity as will cause the maximum in the so-corrected equivalent conductivity values to occur at the lowest concentration at which the error just referred to has attained its constant value. The method of procedure is best illustrated by a reference to the accompanying diagram (Fig. 2). In this the curve AB represents the "observed" values of the equivalent conductivity Λ, of the acid computed from the results of an actual series of experiments (first

[1] For example, it is readily calculated from Kohlrausch's mean values (Wied. Ann., **66**, 794, 1898) of the change of the conductivity at 18° of the ions of neutral salts with the dilution that the mean error in their equivalent conductivity would be 0.42 per cent. at 0.0002 normal and 0.25 per cent. at 0.0005 normal if computed by the method here described, taking 0.0001 as the initial concentration. In the case of the strong acids, whose conductivity changes much less rapidly with dilution, the error from this source would be about one half as great.

series, in nitric acid, p. 381) by subtracting from the observed specific conductivity of the solution $\varkappa_s$ the observed conductivity of the water $\varkappa_w$, and dividing the difference by the concentration C; that is,

$$\Lambda_{obs} = \frac{\varkappa_s - \varkappa_w}{C}.$$

Now the error in the value Λ at A must be at least as great as the ordinate AC, C being equal to the maximum ordinate of AB. If we therefore increase its value by this amount and increase the observed value of Λ of every other point as B' by this amount multiplied by the inverse ratio of the concentrations corresponding

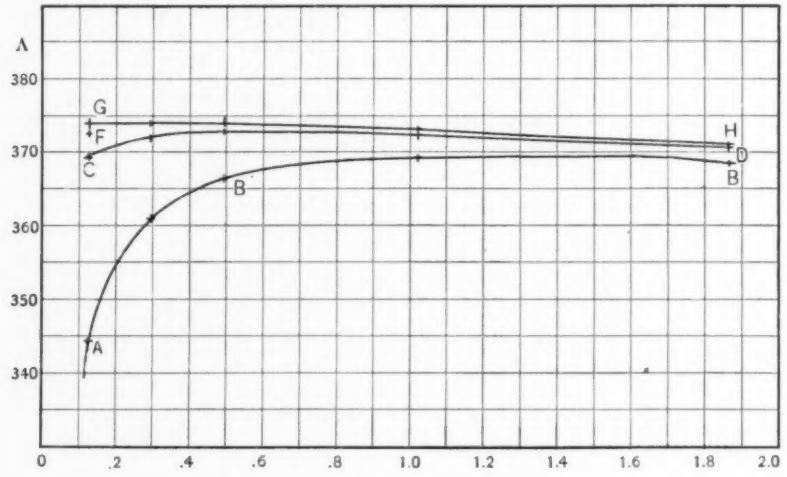

Fig. 2.

to B' and A respectively, a new series of values corresponding to the curve CD is obtained. The value C is still seen to be in error by an amount as great as CF (F being equal again to the maximum ordinate of the new curve CD); the other values on this curve are in error by an amount less in proportion to the greater concentration to which they correspond: we therefore increase all the values in the same way as before, producing a third curve, and this process is repeated till the maximum point on the resulting curve lies on the ordinate through ACF and the curve has the form of GH. This method may also be described algebraically as follows. The true specific conductivity $\varkappa_c$, of the acid (that which it would exhibit in

pure water at any concentration C), is equal to the observed conductivity of the solution $\varkappa_s$, diminished by that of the water $\varkappa_w$, and increased by a quantity δ, constant at all concentrations and equal to the reduction in conductivity produced by mutual influence of the acid and impurities; that is, $\varkappa_c = \varkappa_s - \varkappa_w + \delta$, or expressed in terms of equivalent conductivities,

$$\Lambda_c = \Lambda_{obs} + \frac{\delta}{C}$$

where Λ_c is the true equivalent conductivity of the acid and Λ_{obs} is the "observed" equivalent conductivity as above defined. The value of δ is then determined from this equation by a series of approximations as described above until finally

$$\frac{\delta}{C} = 0$$

and Λ_c coincides with Λ_{obs}.

It should be understood, however, that this method gives only a minimum value for the equivalent conductivity at the highest dilution, for it is only in case the Mass-Action Law equation holds that the conductivity curve approaches asymptotically to a maximum with increasing dilution. If the empirical formula of Kohlrausch $\Lambda_0 - \Lambda_c = KC^{\frac{1}{3}}$ is applicable, the upward slope of the curve must continually increase with decreasing concentration. In fact, Kohlrausch found that the behavior of neutral salts at very low concentrations (0.001 — 0.0001 normal) was intermediate between that required by these two formulas. The values extrapolated with the help of the cube-root formula will therefore give in all probability a maximum limit for the conductivity at the greatest dilution, and the true value will lie between it and that derived by the method just described.

In applying these methods to our results, from 0.06 to 0.1 milli-equivalents per liter was taken as the standard initial concentration, although some measurements and computations have also been made at greater dilutions. The reasons for this selection are: first, that the resistance measurements, owing to a sharper minimum, are considerably more accurate (the average deviation of the separate readings from the mean being less than 0.1 per cent.) than in the

more dilute solution; and secondly, that the computed equivalent conductivities differ when the initial concentration chosen is varied from less than 0.03 to 0.06 millinormal, but that they no longer do so to an important extent when it is varied from 0.05 to 0.1 millinormal, showing that in the 0.03 millinormal solution the maximum influence of the water has not yet been produced.

It will be seen from the data given in the next section that the water used in different series of experiments had a conductivity varying from 0.8 to 1.6×10^{-6}, and consequently, the observed equivalent conductivity at the higher dilutions also exhibit considerable variations. In fact, the latter exist even where different samples of water with the same conductivity were used, showing that the character of the impurities varies and exerts a specific influence. Nevertheless, the corrected values of the equivalent conductivity are substantially identical — a fact which furnishes strong evidence of the correctness of the principle underlying the computations.

The above methods only serve to extend the series of reliable values of the equivalent conductivity of acids from about 0.002 normal down to 0.0002 or 0.0001 normal. To what extent the values at the latter concentration differ from those at infinite dilution can only be estimated. Probably the best basis for this estimate is the assumption of Kohlrausch which is most briefly expressed by the relation:

$$\frac{(\Lambda_\infty - \Lambda_{4000}) \text{ for acids}}{\Lambda_{4000} - \Lambda_{100}) \text{ for acids}} = \frac{(\Lambda_\infty - \Lambda_{4000}) \text{ for salts}}{\Lambda_{4000} - \Lambda_{100}) \text{ for salts}} = \frac{0.9}{3.0}^{1}$$

This method of extrapolation has been applied to our results. Since according to our measurements with hydrochloric acid described in Sections V. and VI. $\Lambda_{4000} - \Lambda_{100} = 377.6 - 369.3 = 8.3$, the so-determined value of $(\Lambda_\infty - \Lambda_{4000})$ for acids is only 2.5 units (or 0.7 per cent.).

V. The Conductivity Data.

The experimental data and the values calculated therefrom will now be presented.

The temperature was in all cases $18.00° \pm 0.02°$. The standard solution of hydrochloric acid used in all the experiments was

[1] Kohlrausch, Wied. Ann., **66**, 794, 1898.

0.009074[1] normal; that of nitric acid was 0.010145[2] normal. The cell constant or capacity of the resistance vessel (that is, the ratio of the specific conductance of any solution to its actual conductance as measured in the vessel) was 0.11659.[3]

The following tables contain the results of the separate series of experiments. As headings are given, the weight in grams (m_w) of water taken, its actual conductance (L_w) multiplied by 10^6 when measured in the vessel, and its specific conductance ($\varkappa_w$) multiplied by 10^6. The first column gives the number of the portions of standard acid or potassium chloride solution which were added; the second gives the total weight of the added portions; the third, the concentration (C) of the resulting solution in milliequivalents per liter (see Section II.); the fourth, the conductance in reciprocal ohms measured in the resistance vessel and multiplied by 10^6; the fifth, the equivalent conductivity of the acid calculated by subtracting from the specific conductance of the solution ($\varkappa_s$) that of the water and dividing the difference by the concentration, *i. e.*, $(\varkappa_s - \varkappa_w)/C$. In the sixth and seventh columns are given the corrected values of the equivalent conductivity computed by the first method described in Section IV., taking for the initial concentration that corresponding to the first and second added portions, respectively. In the eighth column are given the corrected values of the equivalent conductivity calculated by the second method described in Section IV. (In the case of the potassium chloride series these are replaced by the equivalent conductivities obtained by Kohlrausch and Maltby.)

[1] This result was based upon four determinations, of which the data were as follows:

Grams HCl solution taken	346.27	328.60	347.70	356.38
Grams AgCl obtained	0.4506	0.4277	0.4521	0.4623
Equivalent per 1,000 grams sol.	0.009076	0.009078	0.009068	0.009047

The last on account of its great deviation was omitted in taking the mean.

[2] This solution was obtained by dilution (by weight), of a 0.05 normal solution which has been standardized against a 0.1 normal solution of recrystallized barium hydroxide, the titration values showing an average deviation of 0.03 per cent. from their mean. The barium hydroxide was standardized by neutralizing it with nitric acid, evaporating, drying at 170°, and weighing as $Ba(NO_3)_2$, and also precipitating it with sulphuric acid, filtering out, igniting, and weighing the $BaSO_4$. The average deviation from the mean of the four determinations by those two methods was 0.05 per cent.

[3] This was the mean derived from measurements with five distinct 0.01 normal potassium chloride solutions containing 0.7455 grams KCl weighed in air, in 1,000 grams water; the average deviation of the five values from the mean was 0.03 per cent.

HYDROCHLORIC ACID.

$m_w = 163.73$; $10^6 L_w = 11.13$; $10^6 \kappa_w = 1.30$.

Portion No.	Total Weight of Added Portions.	Concentration in Milliequivalents per Liter.	Observed Conductance $\times 10^6$.	Equivalent Conductivity.			
				Water Subtracted.	By First Method. I.	By First Method. II.	By Second Method.
1	0.2248	0.0125	34.82	221.8			420.6
2	2.0305	0.1114	349.34	354.6	371.3		376.9
3	5.0528	0.2717	868.42	367.9	374.8	376.8	376.9
4	8.2065	0.4341	1,390.9	371.3	375.7	377.8	376.9
5	12.9987	0.6689	2,144.8	372.6	375.4	376.1	376.2
6	19.190	0.9574	3,061.0	371.4	375.4	375.7	374.0
	$m_w = 170.96$; $10^6 L_w = 11.95$; $10^6 \kappa_w = 1.37$.						
1	1.3360	0.07036	221.3	346.8			379.6
2	5.4563	0.2806	904.3	370.6	378.5		376.4
3	9.6226	0.4835	1,557.9	372.7	377.0		376.3
4	12.032	0.5966	1,923.8	373.6	377.0		376.4
5	17.928	0.8612	2,775.5	374.1	376.4		375.9
6	37.166	1.6204	5,214.8	374.3	375.4		375.3
	$m_w = 193.83$; $10^6 L_w = 9.41$; $10^6 \kappa_w = 1.10$.						
1	0.5642	0.02634	76.56	297.1			382.8
2	1.2787	0.05947	183.82	341.8	377.2		379.5
3	2.4332	0.1125	354.3	357.4	375.6	374.4	377.5
4	5.0564	0.2307	737.5	367.9	376.8	376.8	377.6
5	7.3384	0.3311	1,062.2	370.7	377.0	376.9	377.3
6	11.162	0.4942	1,588.8	372.6	376.7	376.7	377.0
7	15.184	0.6593	2,119.6	373.1	376.1	376.2	376.3
8	35.180	1.3942	4,489.5	374.6	376.0	375.9	376.2
	$m_w = 184.65$; $10^6 L_w = 7.44$; $10^6 \kappa_w = 0.868$.						
1	2.0218	0.09828	313.9	363.5			378.7
2	3.8508	0.1854	597.8	371.3	379.8		379.4
3	5.7913	0.2760	889.8	372.8	377.7	375.7	378.1
4	8.1604	0.3841	1,238.7	373.7	377.1	376.0	377.5
5	11.665	0.5392	1,741.3	374.9	377.3	376.8	377.6
6	18.636	0.8319	2,678.1	374.3	375.6	375.1	376.1
	$m_w = 184.65$; $10^6 L_w = 7.29$; $10^6 \kappa_w = 0.854$.						
1	0.9254	0.04526	141.28	345.1			371.6
2	2.5137	0.1219	392.35	368.3	381.9		378.3
3	5.4093	0.2583	835.20	373.7	379.8	378.4	378.4
4	7.8974	0.3722	1,201.8	374.2	378.1	376.9	377.4
5	11.571	0.5351	1,728.0	374.9	377.5	376.8	377.2
6	15.715	0.7117	2,298.5	375.3	377.2	376.7	376.9
7	19.915	0.8834	2,848.5	374.9	376.5	375.9	376.2
8	40.055	1.6176	5,208.0	374.8	375.6	375.4	375.5

NITRIC ACID.

$m_w = 181.38$; $10^6 L_w = 13.35$; $10^5 \kappa_w = 1.59$.

Portion No.	Total Weight of Added Portions.	Concentration in Milliequivalents per Liter.	Observed Conductance $\times 10_8$.	Equivalent Conductivity.			
				Water Subtracted.	By First Method. I.	By First Method. II.	By Second Method.
1	0.8480	0.0472	132.1	293.0			374.6
2	2.3534	0.1299	397.0	344.1	373.1		373.9
3	5.4994	0.2985	937.7	360.9	373.4	373.6	373.9
4	9.3059	0.4951	1,568.1	366.1	373.5	373.6	373.8
5	20.477	1.0291	3,273.2	369.3	372.6	372.6	373.0
6	40.940	1.8679	5,922.0	368.8	371.4	371.3	370.8
	$m_w = 175.49$; $10^6 L_w = 13.05$; $10^6 \kappa_w = 1.52$.						
1	1.0421	0.0599	183.7	332.0			374.4
2	3.2765	0.1860	588.9	361.0	374.7		374.7
3	6.5193	0.3634	1,159.7	367.9	374.7	374.8	374.7
4	9.0405	0.4972	1,586.0	368.8	373.8	373.5	373.9
5	14.931	0.7955	2,538.4	370.1	373.0	372.7	373.2
6	20.373	1.0553	3,368.2	370.6	372.8	372.6	373.0
	$m_w = 169.23$; $10^6 L_w = 12.03$; $10^6 \kappa_w = 1.40$.						
1	1.8262	0.1083	337.8	350.6			375.2
2	4.1137	0.2465	782.5	364.4	375.1		375.2
3	7.0453	0.4110	1,306.2	367.9	373.9		374.4
4	12.1903	0.6868	2,190.6	369.8	373.2		373.7
5	19.894	1.0720	3,421.2	370.8	372.9		373.4
6	40.299	1.9550	6,229.7	370.2	371.8		371.6
	$m_w = 183.75$; $10^6 L_w = 12.64$; $10^6 \kappa_w = 1.48$.						
1	1.6063	0.0879	277.1	350.7			372.1
2	3.7972	0.2054	656.0	365.2	373.9		374.1
3	5.8714	0.3141	1,005.6	369.5	375.3	374.8	374.2
4	8.8942	0.4684	1,500.0	370.2	374.6	374.1	374.1
5	14.166	0.7261	2,325.0	369.6	373.9	373.6	372.2
6	20.282	1.0085	3,224.0	371.2	373.1	372.8	372.8
7	40.360	1.8270	5,827.7	371.0	371.9	371.5	372.0

POTASSIUM CHLORIDE.

$m_w = 185.22$; $10^6 L_w = 0.862$; $10^6 \kappa_w = 1.006$.

Conc. Stand. Solution = 0.009990.							Kohlrausch and Maltby.
1	1.2147	0.0651	80.66	129.02			129.16
2	3.5447	0.1876	215.62	128.64	128.52		128.81
3	9.9054	0.5072	565.55	128.06	127.99		128.10
4	20.108	0.9784	1,078.2	127.45	127.46		127.39

In connection with the above data, attention is called to the close agreement in the case of potassium chloride between our values of the equivalent conductivity, given in column five marked "water subtracted," with those of Kohlrausch and Maltby; also to the fact that the application of the first correction method to this neutral salt causes a change of less than 0.1 per cent. in the values of the equivalent conductivity. It will be seen, on the other hand, that, in the case of the acids, both methods of computation raise the equivalent conductivity on an average by about 2 per cent. in 0.25 millinormal, and by about 0.5 per cent. in millinormal solution. Although the values in column five vary quite widely in the different series owing to differences in the quality of the water used, yet when corrected by Method I. they are in substantial agreement in all cases where the concentration corresponding to the first added portion exceeds 0.05 millinormal. The agreement between the results obtained by the two methods has already been considered.

The mean of the "water-subtracted" values at the concentration millinormal (374.0 for hydrochloric acid and 371.4 for nitric acid) are nearly one per cent. lower than the corresponding values earlier obtained by Kohlrausch[1] (377 and 375 respectively). This fact led us to make a new series of measurements on the conductivity of hydrochloric acid at higher concentrations. These were made at 18° in a U-shaped apparatus with a new sample of acid prepared and standardized as before.[2] The dilutions of the stock solution (0.13747 normal) were made by weight and reduced to volume-concentrations at 18°, by means of the specific gravities of water and of the stock solution. On account of the wide range of concentrations measured it was found necessary to use two resistance vessels. The cell constants or capacities of these, determined by five 0.01 normal potassium chloride solutions, were 2.5417 and 8.5370. The average deviation of the separate values from the mean was less than 0.03 per cent. in each case.

The results are contained in the following table. Values corre-

[1] Kohlrausch and Holborn, Leitvermogen der Electrolyte, p. 160.

[2] The analytical data were as follows:

Grams HCl solution taken	112.34	106.58	91.31
Grams AgCl obtained	2.2121	2.0988	1.7994
Equivalents per 1,000 grams sol.	0.13734	0.13734	0.13744

sponding to the round concentrations are summarized in Section VII., page 385.

The values are seen to be only slightly (0.1–0.4 per cent.) lower

HYDROCHLORIC ACID.

$10^6\ L_w = 0.34$. $10^6 \kappa_w = 0.85$. *Cell Constant* = 2.542.

Concentration in Equivalents per Liter.	Actual Conductance $\times 10^6$.	Equivalent Conductivity.[1]	Equivalent Conductivity. (Interpolated from Kohlrausch.)
0.001917	270.12	375.0	376+
0.001937	285.87	375.1	376+
0.004744	697.25	373.1	373+
0.005525	809.79	372.5	372+
0.010124	1,470.8	369.2	370
0.01147	1,661.8	368.2	369+
0.02714	3,878.6	363.4	365
0.03137	4,468.9	362.1	364−
$10^6\ L_w = 0.10$. $10^6 \kappa_w = 0.85$. *Cell Constant* = 8.537.			
0.13747	5600.9	347.8	347+

than those of Kohlrausch. Noyes and Sammet[2] found in $\frac{1}{5}\frac{1}{8}$ and $\frac{1}{2}\frac{1}{5}\frac{1}{2}$ normal solution values 0.5–0.6 per cent. less than Kohlrausch's. The above values were plotted against the cube root of the concentration, and between 0.005 and 0.137 normal were found to lie upon a straight line, the greatest deviation from it being less than 0.1 per cent.

VI. The Corrected Values of the Equivalent Conductivity.

In the following table are summarized the equivalent conductivity values of the dilute solutions computed by both methods from all the series of experiments. The values are interpolated for round concentrations intermediate between those involved in the experiments. In the case of the first method the values computed from the initial concentration corresponding to the first added portion were used, except in the cases where this was less than 0.05 millinormal.

[1] In these values no account is taken of the effect of the water, the correction for which is negligible, except in the first two cases in which the concentration is approximately only 0.002 normal. For this dilution the correction is + 0.2 unit, making the corrected values 375.2 and 375.3 respectively. This correction is taken as one half that computed from the data on page 378 for a 0.001 normal solution.

[2] Journ. Amer. Chem. Soc., **24**, 964, 1902.

It will be seen that the results of the two methods of calculation agree almost completely in the case of both acids. The equivalent conductivity for 0.25 milli-normal hydrochloric acid is 377.6, and for nitric acid of the same strength is 374.4. The difference, 3.2, agrees well with the difference, 3.6, between the conductivities of the Cl and NO_3 ions as derived by Kohlrausch from measurements with neutral salts. It is also of interest to note that the conductivity value extrapolated for 0.25 milli-normal hydrochloric acid

HYDROCHLORIC ACID.

	First Method.						Second Method.					
Conc. Millequivalents.	Separate Series.					Mean.	Separate Series.					Mean.
0.10							376.9	379.1	377.5	378.8	378.3	378.1
0.25	376.8	378.5	376.8	377.7	378.4	377.6	376.9	376.9	377.5	378.2	378.4	377.6
0.50	377.4	377.0	376.7	377.3	376.8	377.0	376.7	376.4	377.0	377.5	377.3	377.0
0.75	376.1	376.7	376.2	375.6	376.5	376.2	375.5	376.1	376.3	376.5	376.7	376.0
1.00	375.7	376.2	376.0		375.8	375.9	373.7	375.8	376.2	375.6	376.1	375.5
1.50		375.6	375.9		375.5	375.7		375.4	376.1		375.6	375.6
	NITRIC ACID.											
0.10							374.0	374.6	375.2	374.1		374.3
0.25	373.6	374.7	375.1	374.5		374.5	373.9	374.7	375.2	374.1		374.3
0.50	373.6	373.8	373.7	374.5		373.9	373.8	373.9	374.2	373.8		373.9
0.75	373.1	373.0	373.1	373.8		373.3	373.4	373.3	373.6	373.4		373.4
1.00	372.6	372.8	372.9	373.1		372.9	373.1	372.9	373.4	372.8		373.0
2.00	371.1		371.8	371.7		371.5	370.4		371.5	371.9		371.3

from those between 0.005 and 0.137 normal under the assumption of the validity of the cube-root formula ($\Lambda_0 - \Lambda_c = KC^{\frac{1}{3}}$) is 381 or only about 0.9 per cent. greater than our corrected valve.

It remains only to apply the estimated correction of + 2.5 units, discussed at the end of Section IV., in order to obtain the most probable values of the equivalent conductivity at infinite dilution. The values so obtained are 380.1 for hydrochloric acid and 377.0 for nitric acid. The values recently derived by Kohlrausch[1] are 383.4 and 379.8 respectively, which differ from ours by less than one per cent. Unless the change with the concentration at very

[1] Sitzungsber. d. konigl. preuss. Akad., 1031, 1901.

high dilutions follows a law radically different from that prevailing at moderate dilutions, it seems certain that these values are substantially correct. The much higher value 395.5 for hydrochloric acid derived by Noyes and Sammet from transference experiments apparently arises from some considerable error, the nature of which still remains to be explained.

VII. Summary.

In this article have been described measurements of the electrical conductivity at 18° of very dilute (0.0001 to 0.002 normal) hydrochloric and nitric acid solutions made by adding to a known weight of water successive portions of 0.01 normal acid. To eliminate the effect of the impurities of the water, two methods of computation of the equivalent conductivity have been used. In both of these, the assumption is involved that the total effect of the acid and impurities on the conductance of each other is produced when a relatively small quantity of acid has been added to the water. The experiments themselves furnish evidence of the correctness of this assumption. In the first method, the increase of the specific conductance over this initial value divided by increase of concentration is regarded as the equivalent conductivity at the higher concentration. In the second method, such a quantity, constant at every concentration, is added to the observed values of the specific conductance as will cause the maximum in the equivalent conductivity values calculated therefrom to occur at the lowest concentration at which the total influence of the acid and impurities on each other has been produced. In spite of considerable variations in the observed conductivities due to the use of different samples of water, the corrected values of the equivalent conductivity derived from different experiments and those computed by the two methods agree well with each other. New determinations were also made at higher concentrations with hydrochloric acid. The final values of the equivalent conductivity (Λ) at various round concentrations (C) in equivalents per liter are as follows:

The values for zero concentration or infinite dilution are extrapolated from those for 0.00025 normal under the assumption that the change between these two limits of concentration stands in the

Concentration in Mols.	Λ_{HCl}	Λ_{HNO_3}	Concentration in Mols.	Λ_{HCl}
0	380.1	377.0	0.005	372.6
0.00025	377.6	374.5	0.010	369.3
0.00050	377.0	373.9	0.020	365.5
0.00075	376.2	373.3	0.030	362.5
0.00100	375.9	372.9	0.050	358.4
0.00150	375.6		0.100	351.4
0.00200	375.3			

same ratio to that between 0.00025 and 0.01 normal as in the case of neutral salts; this ratio having been already derived by Kohlrausch. These values are less than one per cent. lower than those of Kohlrausch and are believed to be substantially correct. That derived by Noyes and Sammet from transference experiments for hydrochloric acid (395.5), on the other hand, is, for some reason as yet unknown, four per cent. higher.

In conclusion the authors desire to express their appreciation to the trustees of the William E. Hale Research Fund for the grant from that fund which enabled this research to be carried out. Also to Professor Noyes for many valuable suggestions received from him in the course of the work.

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THE DISTRIBUTION OF TEMPERATURE IN AN AIR LIQUEFIER OF THE SINGLE-CIRCUIT TYPE.[1]

By W. P. Bradley and C. F. Hale.

THE inquiry which forms the subject of the present paper was undertaken for the purpose of determining the nature of the thermal distribution in the air liquefier recently installed at Wesleyan. This liquefier is of the single-circuit type — that is, all of the air which enters it passes through a single throttling valve and escapes at atmospheric pressure. Its construction has been described in a previous article.

To make the inquiry exhaustive, it would have been necessary to take account of the temperature of both the inflowing and the outflowing air. This type of liquefier is constructed however of tubing so small in diameter that it is practically impossible to measure accurately the temperature of the compressed air, after it has entered the interchanger, without the use of special enlargements in the pipe at the different points whose temperature is desired. These of course could be provided only at the outset, during the winding of the coil. On the other hand, the temperature of the outflowing air, which has expanded to atmospheric pressure, may be determined very simply indeed by inserting thermometers of suitable construction between the discs of the coil.

Though the measurements actually made refer therefore in the first instance to the outflowing air only, they do afford also, as will appear, valuable indications as to the temperature of the inflowing air within the pipes.

Resistance thermometers were used, which were constructed of very pure insulated platinum wire, about 45 cm. in length and .0798 mm. in diameter, wound in the usual way upon narrow strips of mica. They were eight in number, and were calibrated by means of ice, a mixture of solid carbon dioxide and ether, and liquid oxy-

[1] (Contribution from the Cryogenic Laboratory of Wesleyan University.)

gen. They were inserted into the interchanger at different distances from the throttling valve, as follows:

No. 1, between the valve and the lowest disc.

No. 2, between discs one and two, counting upward from the valve.

No. 3, between discs three and four.

No. 4, between discs seven and eight.

No. 5, between discs thirteen and fourteen.

No. 6, between discs twenty-four and twenty-five.

No. 7, between discs thirty-seven and thirty-eight.

No. 8, between discs fifty-seven and fifty-eight, the total number of discs in the liquefier being fifty-nine.

In order not to deflect the outflowing air current unduly, the thermometers were symmetrically distributed about the coil in an ascending spiral. To hold them in place, paraffin was melted upon the mica strips at a convenient spot in such a way that they fitted snugly between the discs when pushed into place. Heavy copper leads were soldered to the ends of the platinum wires, and were brought out at the top of the liquefier and connected with a Wheatstone bridge.

During the tests, the liquefier was supplied with air at 18° C., and at 1,500, 2,000, 2,500 and 3,000 lbs. gauge pressure.

The tests were made in the following manner. The motor and compressor being in normal operation, and the desired pressure having been reached, the valve of the liquefier was opened and so adjusted from time to time as to maintain the pressure practically constant. Great care was taken to make the needed changes of adjustment as minute as possible, in order to avoid unnecessary fluctuations in the volume of the outflowing current. As soon as thermal equilibrium was established in the coil, the resistance of each thermometer was measured. The valve was then adjusted successively to the other pressures, and the thermometer resistances similarly recorded at each. In this way the temperatures of eight different points in the coil were determined for the four pressures named. The results are grouped in the table.

Read from left to right, these figures show very clearly how the cold, expanded air becomes warmed as it passes upward through

TABLE I.

Temperature Readings During the Production of Liquid Air.

Pres.	1	2	3	4	5	6	7	8
1,500	−191	−118	−94	−64	−34	−11	+ 5	+16
2,000	−180	−111	−90	−55	−28	− 4	+ 7	+17
2,500	−189	−104	−85	−48	−23	− 1	+10	+17.7
3,000	−180	−102	−82	−48	−18	+ 5	+14	+18

the coil and approximates more and more the temperature of the inflowing current. One notices at once how very rapidly this thermal interchange occurs at the bottom of the coil, and how comparatively slowly near the top.

Diagram I. in which temperatures are plotted against the heights in the coil which they represent, brings out this fact much more strikingly.

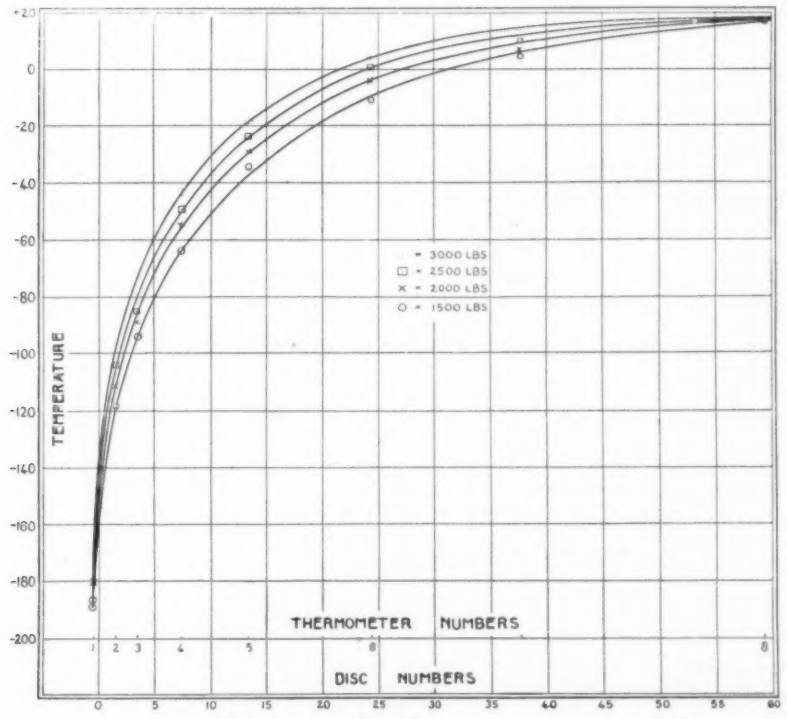


Fig. 1.

If the curve representing the conditions at 3,000 lbs., be taken as an example, the temperature of the air current rises about 80

degrees in passing through a single disc only. The next rise of 80 degrees is secured by traversing the following twelve discs, while the remaining forty-six discs at the top of the coil appear just about sufficient to provide for the last 40 degrees.

To express the same thing in another way, the temperature between the third and fourth discs is almost exactly midway between the temperature of liquid air and that of the inflowing current. Three discs at the bottom effect the same interchange of heat, measured in degrees, as do the upper fifty-six. It was a matter of some surprise to us at the first, that the lowest thermometer, which is entirely below the coil, should not register uniformly the temperature of liquid air. In the light of the facts just stated, the records of this thermometer become intelligible. The thermometer was located indeed below the lowest disc of the coil, but it lay above the expansion valve, and also above six or eight inches of the pipe which connects the lowest disc with the valve. Furthermore, this thermometer lay in the region of eddy currents, as the others did not. These eddy currents consist of a mixture of air directly from the valve, and of air which has been in contact either with the metal parts just mentioned or with the walls of the metal casing which envelops the coil. The temperature of these eddy currents clearly depends on their direction. This in turn depends in part upon the adjustment of the valve, which is determined by the pressure. If the valve happens to deliver its blast directly towards the thermometer, a lower temperature is recorded. If the blast strikes first upon the metallic surfaces, its temperature will be higher on reaching the thermometer.

No such irregularity marks the records of the other thermometers. These are affected only by the steady direct current of air which sifts upward through the disc which happens to lie immediately below them.

From the diagram one may learn also that a decrease in the pressure of the air supplied to the liquefier tends to throw more of the work of thermal interchange upon the higher discs of the coil. Thus, at 3,000 lbs. the temperature of 0° is found near disc No. 22. At 1,500 lbs., the same temperature appears in the neighborhood of disc No. 33. Indeed, complete interchange was

not effected at all at the three lower pressures. Except at 3,000 lbs. the temperature of the outflowing air was uniformly lower than that of the inflow, and the disparity was greatest at the lowest pressure.

This shifting of temperature appears to be due to two causes at least. In the first place, a given mass of air flows more rapidly through the pipes if the pressure be low, owing to its greater volume. The time of exposure is thus lessened and the thermal interchange becomes less complete in a pipe of given length. In the second place, the percentage of liquefaction is less at lower pressures, and in consequence, more of the air supplied to the liquefier returns unliquefied to the compressor. Thus the speed of the outflowing current also is increased. Of course the influence of this factor is comparatively slight.

While it was impracticable, as has been said, to make any direct determinations of the temperatures within the pipes, certain very interesting conclusions concerning them may be drawn indirectly from the data already given. No proof whatever is required for the statement that at any given point in the interchanger the temperature within the pipes is always higher than that outside them. Now it is shown in the table of temperatures already given, that at 3,000 lbs. the temperature of the outflowing current at a point immediately above the first disc is — 102°. As the air at this point has been warmed to its present temperature at the expense of the compressed air which is circulating within the piping of that disc, it is obvious that the temperature of the latter is still higher. But even the outside air is many degrees above the generally accepted value of the critical temperature of air. It would seem therefore to be impossible that liquefaction, in the ordinary sense at least, can occur in this disc, or in fact at any point above the valve.

This conclusion may be still further strengthened. If the very slow interchange of temperature which occurs at the top of the coil be due to the fact that the temperatures of the opposing currents at that level are not far apart, the remarkably rapid interchange at the bottom can only be accounted for by a very marked disparity in this regard. In other words, the air inside the tubing of disc No. 1 is not merely warmer, but is a great deal warmer than that outside at the same level.

It is interesting to note in this connection that if the fall of temperature at the valve is due to the Joule-Thompson effect, as held by Schrötter and Linde,[1] the temperature of liquefaction would be reached by the expanding air, if the temperature just above the valve were as high as — 80°.

Experimental data relative to the question of liquefaction above the expansion valve appear to be very meager. In fact, we have been able to find but one paper which deals at all with the subject from the experimental side — that of Schrötter, already cited. Schrötter presents a diagram showing the progressive change of temperature both immediately above and below the valve of the Linde liquefier, from the beginning of a run, until the establishment of equilibrium and the production of liquid air. At no stage in the operation, as the author takes pains to point out, does the temperature in the pipe, just above the valve, fall below — 120°.

From the theoretical side, this problem has been discussed by Pictet.[2] Travers[3] has expressed the opinion "that no liquefaction actually takes place within the jet, and that the gas, at the moment of its escape is not cooled many degrees below its critical point." The meaning of this is not clear. The facts given above appear to prove that *all* the liquefaction which occurs in a liquefier of the single-circuit type — the type which Travers is discussing — occurs "within the jet," that is, at the valve, at the moment of expansion; and that at the moment of escape, all of the air which passes the valve, whether liquefied or not, is reduced at once to the temperature of liquid air, so soon at least as the production of the liquid has commenced. How liquid air can be produced at all if the air which escapes from the expansion valve into atmospheric conditions "is not cooled many degrees below its critical point" is not easy to see. There is, to be sure, in every liquefier a slight pressure, in excess of the atmospheric, in the expansion chamber around the valve. This slight excess is due to the friction which the returning air meets on its way upward through the coil. In the liquefier here described, this pressure amounts to about 15

[1] Paper read before the Society of German Engineers, 1895. Abstract in Scientific American Supplement, Dec. 21, 1895.

[2] Zeitschrift für comprimirte und flüssige Gase, 7, 1903, 1.

[3] Study of Gases, p. 195.

mm. of mercury. It would certainly prevent the expanding air from falling quite as low as the normal boiling point of liquid air under atmospheric pressure, but could not by any possibility keep it within a few degrees of the critical temperature.

Quite recently E. Erdmann assumes that in the Hampson liquefier there is no formation of liquid except at the valve at the moment of expansion.[1]

As stated above, the progressive change which occurs at the valve of a Linde liquefier at the beginning of a run has already been determined. It seemed desirable to repeat the determination with the present liquefier, so far at least as the returning current is concerned. To this end, temperature readings were taken about once a minute from each of the thermometers Nos. 1–3, from the moment of opening the expansion valve to the establishment of thermal equilibrium. As only one galvanometer and bridge were available however, the records of each thermometer had to be made in a separate run. This accounts for the fact that the initial temperatures are not exactly identical. Before each of the three runs was made, care was taken to see that the coil was of practically uniform temperature throughout. In order to lengthen somewhat the interval of time which elapses before liquid appears, the compressor was run at only 2,000 lbs. pressure and at the low speed of 100 revolutions per minute. Under these conditions no liquid was formed until about nineteen minutes after the opening of the valve. Under the conditions of ordinary running, the period is only eight minutes.

Diagram II. shows with what regularity, in general, the fall in temperature occurred. It is noteworthy however that thermometer No. 1, situated just above the valve, fell very rapidly indeed during the first minute or so. This is easily understood if one considers what would theoretically occur if there were no interchanger at all and the air were to escape through a valve possessing no thermal capacity, against a thermometer which likewise was without thermal capacity. In this hypothetical case, as soon as the valve was opened the thermometer would drop instantly through a certain number of degrees, depending upon the pressure and would then remain constant as long as the air supply was maintained. The curve would

[1] Berichte der deutschen chemischen Gesellschafft, 37, 1904, 195, note 2.

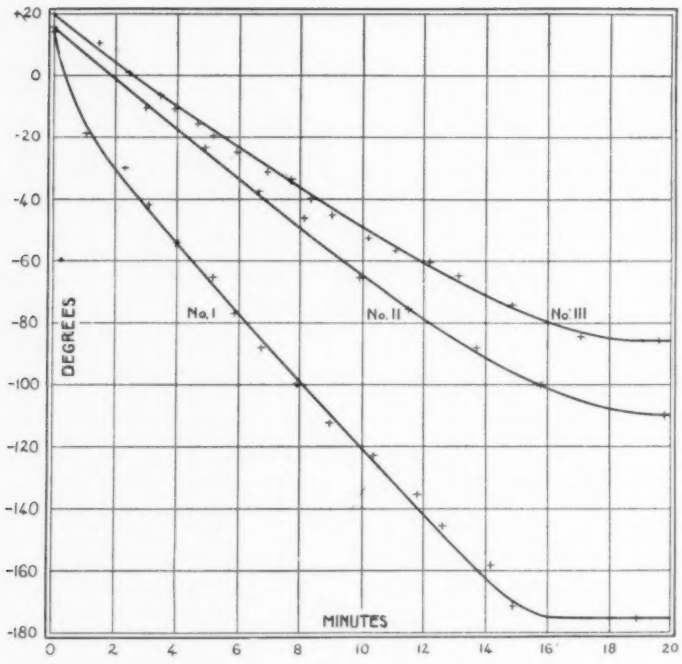


Fig. 2.

consist accordingly of two branches, one of them vertical and the other horizontal, meeting each other at a right angle. In actual practice, the thermal capacity of the valve especially and also of the thermometer, produces a lag, which causes the first branch of the curve to round smoothly into the second, instead of meeting it at an angle. This, of course, is on the assumption that the initial temperature is held constant. The introduction of the interchanger provides for a continuous fall in the initial temperature of the air just before expansion, and so, indirectly, for a corresponding fall in the temperature of the expanded air as it leaves the valve. In other words, the horizontal branch becomes a sloping one and the curve as a whole assumes exactly the form revealed in the diagram. The less the thermal capacity of the interchanger, the more steeply does the second branch fall and the sooner is the liquid formed.

Although, as has been said, no liquid flowed from the drainage pipe of the liquefier in this test for nineteen minutes, the curve of No. 1 shows that the temperature near the valve ceased its rapid

fall after about sixteen minutes. There can be no doubt that liquid was forming at least two minutes before it appeared outside. In fact the actual flow of liquid from the spout was preceded for a minute or so by the appearance of a dense fog. This period of fog undoubtedly represents the time required to cool down to the temperature of liquid air those parts of the casing which lie below the direct influence of the blast, and which serve as a reservoir for the liquid whenever the latter is not drawn continuously, as fast as it is formed.

The curves of Nos. 2 and 3 are much simpler than that of No. 1, and illustrate the effect of the mass of the coils in preventing sudden changes of temperature.

The chief results of this inquiry are:

1. During the production of liquid air in a liquefier of the single-circuit type, the rise in the temperature of the returning current, as it passes upward from the valve through the interchanger, is extraordinarily rapid at the lower end of the interchanger and very slow at the top.

2. During the production of liquid, the compressed air, as it reaches the valve, is not only above its critical temperature, but apparently far above it. No liquefaction occurs inside the pipe.

WESLEYAN UNIVERSITY, MIDDLETOWN, CONN.,
June 17, 1904.

STUDIES OF LUMINESCENCE.

BY E. L. NICHOLS AND ERNEST MERRITT.

IV. THE INFLUENCE OF LIGHT UPON THE ABSORPTION AND ELECTRICAL CONDUCTIVITY OF FLUORESCENT SOLUTIONS.[1]

IT is a characteristic of fluorescent substances that the light emitted during fluorescence is different in color from the light that the substance absorbs and to which its fluorescence is due. This difference may be exhibited graphically by plotting the transmission and fluorescence spectra of the substance in question upon the same diagram, as in Fig. 22. It will be noticed that the brightest

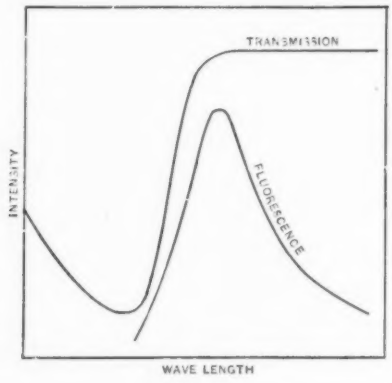


Fig. 22.

fluorescence does not correspond with the region of greatest absorption, but is displaced toward the longer wave-lengths. In all the cases thus far studied by the writers[2] the two spectra overlap, and the fluorescence spectrum extends into the region of strong absorption. But it can also be followed for a considerable distance beyond the extreme infra edge of the absorption band. A fluorescent sub-

[1] A preliminary account of the experiments described in this paper was presented to the American Physical Society at the Washington meeting, April 22, 1904. An abstract appeared in the PHYSICAL REVIEW, Vol. 18, p. 447, June, 1904.

[2] PHYSICAL REVIEW, Vol. 18, p. 403, and Vol. 19, p. 18.

stance is thus able to emit light which, under ordinary conditions, it does not absorb; and no simple relation between absorption and emission can be recognized. In consequence of this fact fluorescent substances are usually excepted from the application of Kirchoff's Law.

This seeming lack of a simple relation between absorption and emission has made it difficult to form a picture of the molecular processes that accompany fluorescence. For, whatever may be the condition of the fluorescent substance, it does not seem possible that its molecules can be in the state of vibration corresponding to the fluorescence spectrum without also possessing the power of absorbing by resonance the same rays that they emit. In seeking an explanation of this difficulty it must be remembered that absorbing power is usually determined when the substance under investigation is *not* excited to fluorescence. The absorbing power *during* fluorescence may be quite different, for it seems not improbable that the same rays that excite fluorescence also produce a temporary change in absorbing power of a fluorescent substance. If such a change really occurs the difficulty mentioned above may prove to be only an apparent one, and the absorption, as determined during fluorescence, may be found to bear to the emission spectrum a relation which is at least similar to that called for by Kirchoff's Law.

A change in absorbing power during fluorescence has been observed in the case of uranium glass by Burke,[1] who found a considerable increase in the absorption when the glass was brightly fluorescent.

The writers have recently undertaken a study of the effect of fluorescence upon absorption in the case of other fluorescent substances, and have detected a well marked increase in absorbing power during fluorescence in each of the three substances thus far tested. The methods employed and the results obtained are described in the first part of the present paper. In attempting to interpret the results of this investigation we were led to suspect that fluorescence is accompanied by a temporary dissociation of the active molecule or ion, similar perhaps to the dissociation produced in gases by the action of Röntgen rays, and that the change in absorp-

[1] John Burke, Philosophical Transactions, Vol. 191A, p. 87, 1898.

tion during fluorescence is due to the presence in the solution of the products of this dissociation.[1] Since such dissociation would in all likelihood bring about an increase in electrical conductivity, it seemed desirable to study the possible influence of light upon the conducting power of fluorescent solutions. The negative results obtained by those who had previously attempted to detect a change in conductivity in solutions due to illumination showed that such an effect, if present at all, must be quite small. We have, however, obtained conclusive evidence of an increase in electrical conductivity during fluorescence in the case of each of the five substances thus far tested. The second and third parts of the paper are devoted to a description of the experiments on this subject and a statement of the considerations which led us to undertake them.

I. The Influence of Fluorescence Upon Absorbing Power.

In the experiments of Burke, to which reference has already been made, the light used was that due to the fluorescence of a piece of uranium glass, and the absorption of the rays from this source by a second piece of uranium glass was determined photometrically. The absorption was found to be increased nearly 50 per cent. when the second piece of uranium glass was excited to bright fluorescence. While the method employed by Burke is a sensitive one, and well adapted to demonstrating the existence of the effect sought, it does not lend itself readily to a detailed study of the subject. It appeared to us desirable to determine not only the increase in total absorption, but also the influence of fluorescence on the form of the absorption spectrum. With this object in view we have determined the change in absorbing power for a number of different wave-lengths throughout the region in which the effect was observable, using for this purpose a Lummer-Brodhun spectrophotometer. Three fluorescent solutions have thus far been tested, namely, fluorescein in water, eosin in alcohol, and rezazurin in alcohol. Each of these solutions showed an increase in absorbing power during fluorescence, the effect being most marked in the case of fluorescein. For this reason the study of the subject has

[1] The dissociation here considered can hardly be of the usual electrolytic type, for it seems to be well established that with many substances fluorescence is an ionic property, and can be excited only after electrolytic dissociation has already occurred.

been carried further in the case of the latter substance than with either of the other two.

The arrangement of apparatus is shown in Fig. 23. The fluorescent solution, contained in a rectangular glass cell, *C*, was placed in front of the slit of the collimator. The solution was excited to fluorescence by rays from the source *E*, which usually consisted of a bank of four acetylene flames. When it was desired to measure the absorption of the solution without fluorescence a screen was interposed between *E* and *C*. A block of magnesium carbonate, *M*, reflected a portion of the light from *E* through the cell containing the fluorescent solution into the collimator slit, *S*. By altering the distance of *M* from *S* the transmitted light could be adjusted to any desired intensity. In some of our earlier experiments the block of magnesium carbonate was removed and direct sunlight was used. The comparison source was an acetylene flame, *A*, whose rays were reflected from a second block of magnesium carbonate, *M'*. The spectrophotometer was used in the ordinary way, *i. e.*, without a lens in the eye piece.

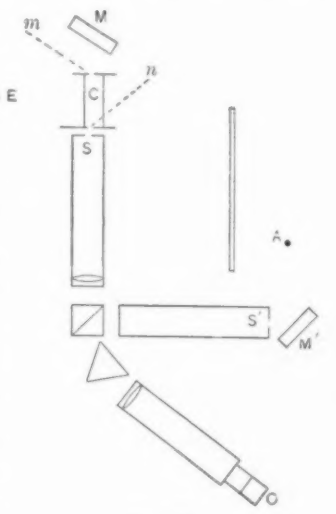


Fig. 23.

To determine the increase in absorption due to fluorescence the following three readings were required for each wave-length studied:

1. *Transmission* (*T*).—An opaque screen was placed between *E* and *C* to prevent fluorescence. The slit *S'* was then opened or closed until the two parts of the field, as seen from *O*, appeared equally illuminated. The width of the slit, as read from the drum of its micrometer screw, was then proportional to the intensity of the transmitted light. We shall designate this reading by *T*.

2. *Fluorescence* (*F*).—The screen was removed from between *E* and *C* and placed between *C* and *M*, so that the only light reaching the slit was that due to the fluorescence excited by the rays from *E*. The setting of *S'* for equal illumination was then a measure of

the intensity of fluorescence for the particular spectral region studied.

3. *Transmission and Fluorescence Combined* (C).—Both screens were removed. In this case the light entering the slit consisted partly of rays from M which had been transmitted by the solution and partly of rays originating in the solution itself by fluorescence.

The width of the slit S remained the same during all of the above readings.

If the absorbing power of the solution is not altered by fluorescence it is clear that the sum of the first two readings should be equal to the third except for accidental errors of observaton. But if fluorescence brings about an increase in absorbing power this equality can no longer hold; for, while the amount of light reaching the slit due to fluorescence will be the same in the third measurement as in the first, the light from M, which must pass through the cell, will be less intense than that observed without fluorescence. In this case therefore $F + T$ is less than C. In fact C may be looked upon as the sum of two parts F and T', where T' is the amount of light from M that is transmitted by the solution when the latter is excited to fluorescence. Since $F + T' = C$ we have

$$F + T - C = T - T'.$$

The quantity $F + T - C$ is therefore a measure of the increase in absorption due to fluorescence.

A single determination of the increase in absorption thus requires three photometric settings, each of which is subject to the usual accidental errors of observation; and the quantity sought, which is in all cases small, is obtained as the difference of two quantities that are relatively large. The results will therefore be largely affected by errors, whether accidental or systematic, in the individual readings. For this reason it was necessary to consider the possible sources of error with especial care. The recognized sources of error and the means taken to avoid them are discussed below.

Errors of Observation.—In order to reduce the effect of accidental errors each set of readings was repeated several times. In some cases as many as ten settings were made for each of the three quantities T, F, and C. The advantage to be gained by repetition was limited, however, by eye fatigue and the resulting loss of sensi-

tiveness. In making a series of determinations extending throughout the spectrum we found it inadvisable to repeat the settings more than four times. The settings were usually made by one observer, while the indications of the micrometer screw were read and recorded by the other.

Fluctuations in the Source of Light.—In our early experiments intense fluorescence was obtained by the use of the arc as an exciting source. Unfortunately the irregular fluctuations were found to neutralize entirely the advantage of great intensity. Sunlight was equally unsatisfactory. In most of our work a bank of acetylene burners was used to excite fluorescence, and with this source no further trouble due to variations in intensity was noticed.

Stray Light. — The effect of this source of error will depend upon the origin of the stray light and the manner in which it enters the instrument. Light reflected into the slit S by dust particles in the cell will cause no error in the final result; for the effect of light due to this cause will be to increase C and $T + F$ by equal amounts. Stray light from E which reaches the slit by any other route will be equally harmless, provided it is suppressed by the screen between E and C (Fig. 23) during the measurement of transmission. But light reaching the interior of the instrument in such a way as to remain nearly constant during the measurement of T, F, and C may lead to serious error. In this case each of these three readings will be too large, and the quantity $T + F - C$ will be in error by the amount of the stray light. To prevent any stray light from entering the instrument through the slit S opaque screens were arranged as shown, in part, in Fig. 23. The purpose of the large screen was to cut off all light from the comparison source. The cell C was completely covered with black paper with the exception of the face toward E and the two narrow openings, m and n, for the transmitted light. To prevent light entering the telescope after diffuse reflection from the prisms the whole instrument was covered with several layers of dark cloth, while screens were so placed as to prevent the direct rays from E or A (Fig. 23) from reaching any part of the spectrophotometer. The experiments were performed in a room with black walls, the only light in the room being that from the flames used in the measurements. After these precautions

were taken it was found that when screens were placed between E and C and between M and C no trace of light could be detected in the spectrophotometer field. We feel confident therefore that the errors due to stray light are very small.

Zero Point. — The zero point of the micrometer screw used in measuring the width of the slit S' was determined by placing an acetylene flame immediately in front of the slit, so as to illuminate it brightly, and then closing the slit until no light could be detected. It is clear that an error in this zero point would make each of the readings T, F, and C incorrect by the same amount, so that the result $T + F - C$ would be subject to the same error as that made in determining the zero point. The setting for zero point was repeated many times, and the agreement of the different readings was such as to convince us that the error could not exceed half a division.

Other less important sources of error, such as irregularities in the screw, "lost motion," etc., require no special discussion.

Dependence of Fluorescence Absorption upon the Intensity of the Incident Light.

In attempting to obtain the most favorable experimental conditions for studying fluorescence absorption (*i. e.*, the increased absorption due to fluorescence), we were at first led astray by assuming that absorption in a fluorescent solution takes place in accordance with the same laws that hold in ordinary optically perfect media. We expected that the effect of fluorescence would be to increase the *coefficient of absorption* without altering the usual exponential law. If this were true the percentage absorption would be constant for a given solution and a fixed intensity of fluorescence, while the actual amount of light absorbed would increase with the intensity of the incident light. If aI is the absorption under ordinary conditions, $a'I$ the absorption during fluorescence, and I the intensity of the incident light we have

$$T = I(1 - a) \qquad T' = I(1 - a')$$
$$T + F - C = T - T' = I(a' - a).$$

The quantity determined by our measurements is therefore

$I(a' - a)$, and, *if a' is independent of I*, it is clear that the best experimental conditions are attained when both the fluorescence and the incidence light, I, are made as great as possible.

Our early experiments, in which the conditions were chosen in accordance with the considerations just stated, gave results that were often discordant. For example, a preliminary set of readings, which happened to be made with I rather small, had indicated a well-marked increase in absorption; *i. e.*, the difference between C and $T + F$ was a large fraction of T. With the expectation of making the difference greater, and so increasing the accuracy of the determinations, the measurements were repeated with the intensity of the incident light largely increased. To our surprise the difference between $T + F$ and C was no larger than before. In fact, the errors of observation sometimes made it appear questionable whether there was any change at all due to fluorescence. We were at first inclined to ascribe the unsatisfactory results to irregular fluctuations in the intense sources of light that were used in our early experiments. But even after we had been forced to abandon the sun and the electric arc as sources, and had adopted acetylene flames throughout, no gain resulted from increasing the intensity of the incident light.

A series of measurements undertaken to determine the dependence of the effect studied upon the intensity of the incident light has since convinced us that the absorption of light in a fluorescent solution does not occur in accordance with the usual laws of absorption. The results of this series of measurements are contained in Table I. It will be observed that the quantity $T + F - C$ is nearly constant for all values of T; the variations are no greater than the possible errors of observation. Since T is proportional to I, we must conclude that the percentage absorption is not independent of I, but increases as I is made smaller. The total amount of energy absorbed, however, is constant throughout the range studied. It appears that when the solution is excited to fluorescence it acquires the power of absorbing a certain definite amount of energy, in addition to that absorbed under ordinary conditions, from a beam of light passing through it. The amount absorbed doubtless depends upon the intensity of fluorescence, the wave-

length of the light, and other factors; but our observations all point to the conclusion that it does *not* depend upon the intensity of the transmitted beam.

TABLE I.

Dependence of Fluorescence Absorption Upon the Intensity of the Incident Light. The measurements were made at wave-length 0.535 μ.

Transmission. T	Fluorescence. F	Transmission and Fluorescence Combined. C	Fluorescence Absorption. $T+F-C$	Percentage Fluorescence Absorption. $\frac{T+F-C}{T}$
18.4	34.6	46.3	6.7	36.4
34.9	34.6	64.2	5.3	15.2
61.0	34.9	91.2	4.7	7.7
12.9	34.5	42.0	5.4	42.0
24.7	34.6	52.8	6.5	26.3
12.7	33.8	41.5	5.0	39.4

It was unfortunately not practicable to investigate the effect for values of T still smaller than the smallest in Table I., for with such feeble illumination of the spectrophotometer field accurate settings became impossible. It is clear, however, that the quantity $T+F-C$ cannot remain constant for very small values of T; for this would mean that the energy absorbed on account of fluorescence is greater than the total energy of the incident light. It appears to us probable that something analogous to saturation occurs in the case of fluorescence absorption. As the intensity of the incident light is gradually increased from zero, the absorption due to fluorescence probably increases also until a certain maximum is reached, after which a further increase in the intensity of the incident light produces no change in the fluorescence absorption.

Relation between Fluorescence Absorption and Intensity of Fluorescence.

Although there is every reason to expect that the absorption due to fluorescence will be greater when the fluorescence is more intense, the lack of a theory of fluorescence makes it impossible to predict the quantitative relation between the two phenomena. With the object of determining this relation experimentally we have measured the fluorescence absorption of a solution of fluorescein at 0.535 μ for several different intensities of fluorescence. The fluorescence was varied by

altering the distance between the cell C (Fig. 23) and the exciting source E. By altering the position of the block of magnesium M (Fig. 23) the intensity of the transmitted light was adjusted in each case to approximately the same value.

The results are shown graphically in Fig. 24. In spite of the fact that each point plotted represents the average of several determinations, the curve obtained is far from being a smooth one. The results are nevertheless sufficient to show that fluorescence absorption is not directly proportional to the intensity of fluorescence. Here too we have to deal with something analogous to saturation. Although further experiments will be necessary to establish the

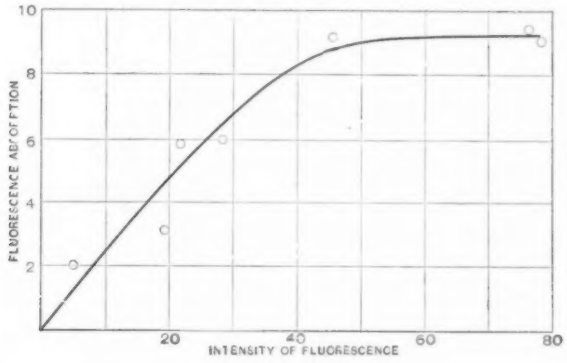


Fig. 24.

exact relation between fluorescence and fluorescence absorption, numerous observations incidental to other phases of the present investigation serve as confirmation of the general form of the curve shown in Fig. 24.

Fluorescence Absorption as a Function of Wave-Length.

In the experiments thus far described the measurements were always made in some one region of the spectrum. The wave-length of the light used, having been chosen by trial so that the fluorescence absorption was well marked, was kept constant during the whole series of determinations. To determine the florescence absorption for different wave-lengths the telescope of the spectrophotometer was shifted so as to bring different regions of the spectrum into the field, and several observations of T, F, and C were made

for each position. During these determinations the intensity of the light exciting fluorescence and the intensity of the light used for the measurement of transmission were kept as nearly as possible constant.

TABLE II.

Dilute Solution of Fluorescein. Observations to Determine Typical Fluorescence, f, and Fluorescence Absorption, A_F. Thickness of Absorbing Layer 4.9 *cm.*

Wave-Length.	T	F	C	A_F	A_F Corrected.	f Computed.
.512μ	18.1	25.9	34.3	9.7	9.5	31.6
.518	19.8	27.4	40.9	6.3	8.5	32.0
.525	22.3	26.2	41.0	7.5	6.7	29
.539	27.2	20.7	43.3	4.6	4.7	20.7
.555	27.2	15.0	39.0	3.2	3.2	15
.506	12.9	20.2	24.4	8.7	7.7	28.6
.500	8.6	12.2	17.3	3.5	3.5	20.5
.494	6.5	7.4	13.4	0.5	0.5	13.8

The results of a series of observations of this kind in the case of fluorescein are given in Table II. The solution chosen for these experiments was quite dilute, preliminary experiments having shown

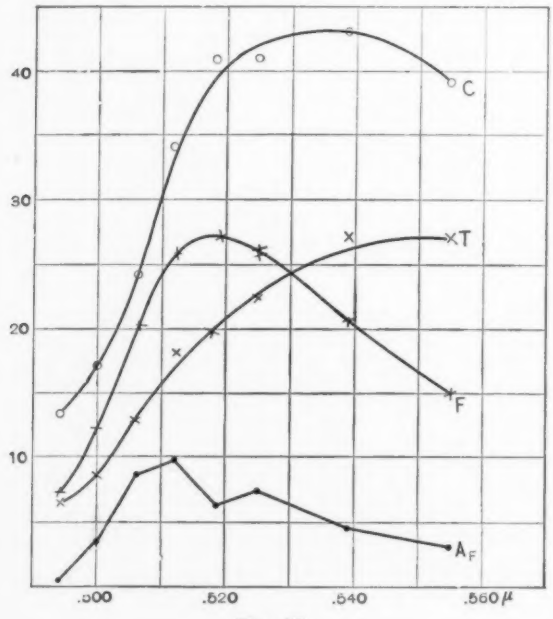


Fig. 25.

that it was difficult to obtain reliable results with more concentrated solutions, especially in the neighborhood of the normal absorption band. The data given in Table III. for T, F, C, and A_F are shown graphically in Fig. 25, the vertical scale being the same for all four curves.

In the case of observations made under constant conditions we should expect the successive readings for F, T, and C to lie upon smooth curves; and it is natural to ascribe any irregularities that appear to accidental errors. Acting upon the assumption that the conditions were constant during the observations plotted in Fig. 25,

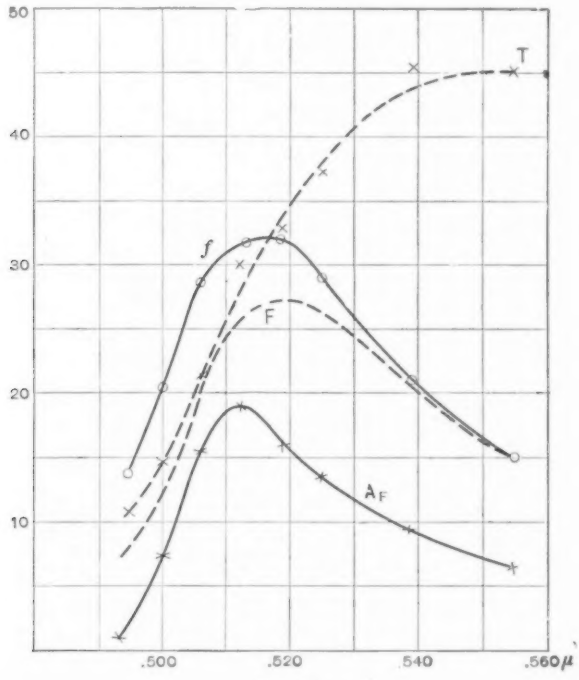


Fig. 26.

we have drawn smooth curves for T and C, as shown in the figure. By using in the computation of A_F the values of T and C that are given by these curves we obtain a curve for fluorescence absorption which is largely free from the irregularities due to accidental errors. The curve obtained in this way is plotted (to a different scale) in Fig. 26. Such a procedure would not be justified

if the irregularities in the curves were due to fluctuations in the source of light or to any similar cause. But the smooth curve obtained for F, without adjustment, affords strong evidence that the experimental conditions were really steady, and that the irregularities in the other two curves are due to errors of observation. It has been our uniform experience that accidental errors are more common in the settings for T and C than in those for fluorescence.

In spite of the irregularities in the curve for fluorescence absorption in Fig. 25 a general resemblance will be noticed between this curve and that for fluorescence (F). In the case of the smooth curve for A_F the resemblance is still more marked. This similarity in form has also been noticed in the curves plotted from numerous other sets of observations, both with fluorescein and with eosin, although it was often made less striking by our inability to keep all the conditions constant during the determination of a complete curve.

It seems probable that this resemblance between the curves for F and A_F corresponds to some real and intimate connection between fluorescence and fluorescence absorption; apparently we have to deal not with two separate effects produced in the solution by the action of the exciting light, but rather with two different manifestations of the same molecular process. If this is true we should expect the relation between the two phenomena to be more clearly brought out by a comparison between the curve for fluorescence absorption and the typical fluorescence spectrum for the solution. The latter curve depends only upon the nature of the solution and the intensity of the exciting light, while the form of the fluorescence spectrum directly observed is modified by absorption and therefore depends upon the thickness of the solution and the method of observation.[2] The relation between the typical fluorescence, f, and the observed fluorescence, F, may be derived as follows:

Let the face of the cell containing the fluorescent solution be uniformly illuminated by the exciting light, so that all portions of the solution lying between m and n (Fig. 23) are equally fluorescent. In this case light is emitted in the direction of the slit S by all portions of the solution lying between m and n. Let f be the

[1] See Figs. 4, 5 and 6 in our second paper, PHYSICAL REVIEW, XVIII., p. 403.

amount of light of a given wave-length that is emitted in this direction per centimeter. The curve that shows f as a function of the wave-length is what has been called the typical fluorescence spectrum.

The light proceeding in the direction toward S will be of increasing intensity as we pass from m to n. If its intensity at a distance x from m is I, we have

$$dI = fdx - aIdx$$

where a is the coefficient of absorption. Upon integrating this equation we have

$$I = \frac{f}{a} + K\varepsilon^{-ax}.$$

The constant of integration K is determined by the fact that when $x = 0$, $I = 0$, so that

$$K = -\frac{f}{a}.$$

Therefore

$$I = \frac{f}{a}(1 - \varepsilon^{-ax}).$$

The light entering the slit, which determines the measured fluorescence F, is the value of I for $x = l$, where l is the thickness of the solution.

$$F = \frac{f}{a}(1 - \varepsilon^{-al}).$$

$$f = \frac{aF}{1 - \varepsilon^{-al}}.$$

Since a is readily computed from the measurements of transmission we are thus able to compute the typical fluorescence from the observed fluorescence F. In the case of the experiments corresponding to Fig. 25 the percentage transmission is most conveniently computed by dividing the value of T for the wave-length in question by the value of T for $\lambda = 0.555\ \mu$. The latter point on the curve for T lies outside the absorption band, so that the transmission of the solution is complete. If the percentage transmission be denoted by θ

$$\theta = \varepsilon^{-al},$$

$$\log \theta = -al,$$

$$f = -\frac{F \log \theta}{l(1-\theta)}.$$

The typical fluorescence spectrum computed in this way is shown in Fig. 26. A comparison of this curve (f) with the smoothed curve for A_F adds support to the view that the phenomena of fluorescence and fluorescence absorption are intimately connected. But the relation between the two does not appear to be a simple one. Unless the observations are effected by more serious errors than we have any reason to suspect, the results show that fluorescence absorption does not bear a constant ratio to the intensity of the fluorescence with which it is associated. And yet this simplest possible relation between the two phenomena is the one which it seems most natural to expect. We are of the opinion that the question of the exact relation between the two curves is one which requires further experimental investigation before it can be looked upon as definitely settled.

A series of observations like those just described was made with a still more dilute solution of fluorescein with results that agree, in the main, with those stated above. In these experiments sunlight was used to excite fluorescence. The variations in the intensity of this source made it impossible to apply the method of smoothing described above; and without some means of reducing the effect of accidental errors the results were too irregular to lead to any reliable conclusions. These observations, therefore, serve merely as a check upon the general form of the curves shown in Fig. 25. The same statement may be made with reference to numerous other observations in which we were unable to maintain constant conditions throughout the complete series of readings.

In Fig. 27 we have plotted the results of a series of measurements made with a more concentrated solution of fluorescein. It will be noticed that the edge of the absorption band is much steeper than in Fig. 25, and the band extends further toward the red. Although the curve for fluorescence absorption (A_F) is similar in form to that shown in Fig. 25 its maximum is displaced toward the

longer wave-lengths. It is clear that the normal absorption of the solution exerts a modifying influence upon the increase in absorption which accompanies fluorescence.

In addition to the experiments with fluorescein a few measurements were made also with alcoholic solutions of eosin and resazurin. In the case of the latter substance the measurements were

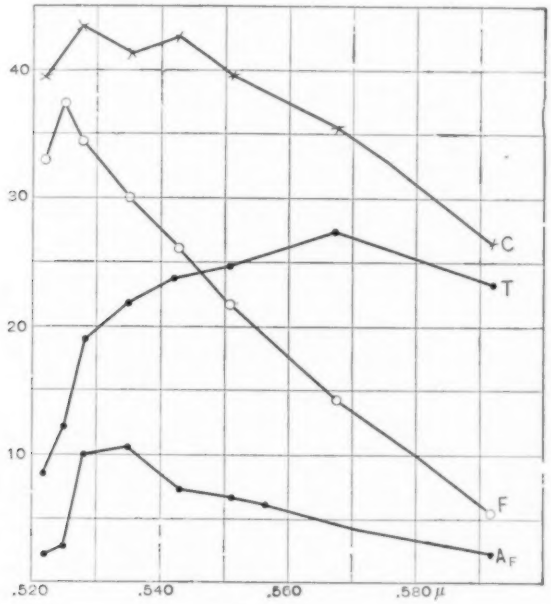


Fig. 27.

made for only a few wave-lengths, and served merely to show that the effect was present. With eosin a nearly complete curve was obtained, although not under entirely satisfactory conditions. The curve was the same general character as those obtained with fluorescein, and occupied the same position with relation to the absorption band.

II. Theoretical.

Throughout the progress of the experiments that have been described in the present paper and in those which precede it we have naturally tried to form some picture of the underlying mechanism of the phenomena studied. It is perhaps needless to say that serious difficulties have been encountered; but although we have

not succeeded in forming a wholly satisfactory picture of the molecular processes involved in fluorescence, the considerations stated below have nevertheless led us to the adoption of a working hypothesis regarding the general character of these processes which has been of considerable assistance.

In attempting to form a theory of fluorescence it is natural to turn to the other, and in some respects simpler cases of luminescence for assistance; for it is difficult to believe that the many resemblances noticeable between luminescence phenomena of different types are merely superficial. In the case of several classes of luminescence phenomena the first steps in the development of a theory have fortunately already been taken. Thermo-luminescence, for example, has been explained as the result of some chemical change in the luminescent substance, during the progress of which the molecules are thrown into such violent vibrations as to bring about the emission of light. Luminescence ceases in such cases when the change has been completed; and some outside stimulus is required, such as that furnished by cathode rays, to restore the substance to the sensitive state. Not only in this explanation of thermo-luminescence a plausible one but in several instances conclusive evidence has been found that the assumed change really occurs.

A somewhat similar suggestion has been made by E. Wiedemann in the case of phosphorescence. According to this view some change is produced in the phosphorescent substance by the action of the exciting light, and the gradual restoration of the original condition after the excitation has ceased is accompanied by luminescence. Although it has not yet been possible to determine the exact character of the assumed change, or even to demonstrate by direct tests that such a change occurs, the view suggested by Wiedemann has undoubtedly been an important aid in the more recent study of phosphorescence.

If, as seems not unlikely, the difference between phosphorescence and fluorescence is chiefly one of the duration of luminescence, the hypothesis just stated may be applied to the latter class of phenomena without essential modification, and we may assume that fluorescence is also due to some temporary change in the fluores-

cent substance. We must assume further that the return to the original condition is almost instantaneous; so that luminescence persists for only an inappreciable time after the removal of the exciting cause. According to this view fluorescence involves two processes (1) the alteration in the fluorescent substance brought about by the exciting light; (2) the spontaneous return of the modified substance to its original state. These two processes occur simultaneously; and one or both must be accompanied by the emission of light.

This view lends itself readily to an explanation of the increase in absorption that accompanies fluorescence, for it is clear that during the progress of such a change as is here assumed the substance may possess properties that are entirely different from those of the original substance. It is natural also to expect some intimate connection between fluorescence and fluorescence absorption, for the increased absorption during fluorescence is doubtless due, at least in part, to the same molecules or atoms whose vibrations bring about the emission of light. Without more detailed assumptions regarding the nature of the change produced by the exciting light it is not possible to predict the laws of fluorescence absorption, *e. g.*, the dependence of the effect upon wave-length, intensity of fluorescence, etc. But, on the other hand, the experimental study of these laws will afford a firm foundation for the further development of the working hypothesis.

The considerations which make it natural to expect a change in absorption during fluorescence apply equally well to all cases of luminescence in which there is a change in the active substance during excitation and a return to the original state during luminescence. We should therefore expect a change in absorbing power in the case of thermo-luminescence, chemi-luminescence, and phosphorescence. In fact, it seems not improbable that some modification of Wiedemann's original hypothesis may be found to be applicable to *all* classes of luminescence, and in this case we should expect every type of luminescence to be accompanied by a change in absorption. So far as we are aware, no experimental study of absorption during luminescence has been undertaken except in the case of fluorescence.

A hypothesis which assumes that luminescence results from some chemical or physical change in the luminescent substance evidently implies not only a change in absorbing power during luminescence, but also temporary alteration in the other properties of the substance. The study of these changes, if such are found to occur, offers a promising means of attacking the general problem. This field of investigation also appears to be practically untouched.

It has generally been assumed, by those who regard Wiedemann's suggested explanation of phosphorescence and thermoluminescence with favor, that the change accompanying luminescence is of a chemical nature. Various suggestions have been made regarding the character of the reactions produced by the exciting light (or other cause), and attempts are not lacking to trace a connection between luminescence and chemical constitution. It appears to us that it is desirable to take into consideration changes of a different kind, which do not involve, necessarily, any chemical action. The simplest change of this kind is dissociation. In cases of photoluminescence this is just the effect that we should expect the exciting rays to produce. We can scarcely doubt that the absorption of the exciting light is the result of resonance on the part of the molecules or atoms of the active substance; and although the vibrational energy thus imparted to the molecules is rapidly transformed by collisions into translational energy (heat) yet under favorable conditions the molecules might be thrown into such violent oscillation as to be torn apart. Since chemical activity is usually increased by dissociation, chemical changes of the usual kind might occur as a secondary effect. Many instances of increased chemical activity due by the action of light on fluorescent substances might be cited.

If we look upon light as an electromagnetic phenomenon we should expect the vibrations produced by the exciting rays to be such as tend to separate the positive and negative parts of the molecule, and the resulting dissociation would either be of the usual electrolytic type or similar to that produced in a gas by the action of Röntgen rays. In the case of fluorescence the latter type of dissociation seems most probable; but in either case, if the view outlined above is correct, fluorescence should be accompanied by an

increase in the electrical conductivity of the fluorescent substance. It was in order to test this conclusion that the experiments described in the third section of this article were begun. A more detailed discussion of the hypothesis outlined above, and of the experimental facts which tend to confirm it, is reserved for a later communication.

III. The Influence of Fluorescence upon Electrical Conductivity.

The effect of light and Röntgen rays upon the conductivity of solutions has been tested by Cunningham,[1] in the case of five solutions, one of which, namely, uranyl nitrate, was fluorescent. In the experiments with light an arc containing iron was used as a source, and the solutions were contained in a cell having a quartz window, the object being to obtain intense ultra-violet rays. Although some indication of increased conductivity was observed, the observations were rendered so uncertain by the heating effect of the rays from the arc that the author did not regard the results as reliable.

Experiments of a similar character were undertaken by Regner[2] with especial precautions against the disturbances due to the heating effect of the source. No change in conductivity as great as 0.1 per cent. could be detected, although the substances tested included those for which Cunningham had found indications of a positive result. Several fluorescent substances were tested by Regner, also with negative results.

In the paper by Burke[3] on the change in absorption due to fluorescence, mention is made of preliminary experiments upon the conductivity of fluorescent substances; but the author states that difficulties were met with which led him to abandon these experiments and to take up the study of absorbing power instead.

Our own experiments upon this subject were undertaken with the feeling that the increase in conductivity due to fluorescence was probably very small, comparable rather with the conducting power

[1] J. A. Cunningham, "An Attempt to detect the Ionization of Solutions by the Action of Light and Röntgen Rays," Proc. of the Cambridge Philosophical Society, Vol. 11, p. 431–3 (1902).

[2] Physikalische Zeitschrift, 4, 862, 1903.

[3] Burke, l. c.

produced in gases by the action of Röntgen rays than with ordinary electrolytic conductivity in solutions. In attempting to detect so small an effect it seemed advisable to work with solutions in which the normal conducting power was as small as possible. In the case of all the substances thus far tested we have therefore used absolute alcohol as a solvent.[1]

The accurate measurement of the resistance of alcoholic solutions offers considerable difficulty; for while the conducting power is too great to permit the employment of an electrometer method, such as would be used with gases, it is too small to be determined with accuracy by the methods that are generally used with aqueous solutions. No benefit was to be gained in the present experiments by increasing the cross section of the liquid tested, and so reducing its resistance; for if the thickness exceeded a rather small value the absorption of the liquid made it impossible to excite the whole mass to fluorescence. After trying a number of different methods without satisfactory results we abandoned the attempt to accurately measure the total resistance, and directed our attention to the measurement of the *change* in resistance due to illumination. The most satisfactory method that we have found for this purpose is that of the ordinary Wheatstone bridge, using a direct current and a galvanometer of high resistance.

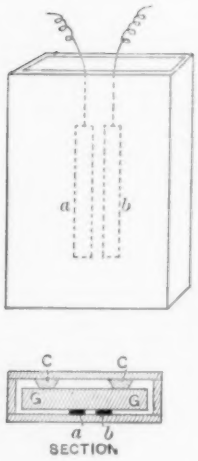


Fig. 28.

The form of the cell used to contain the fluorescent solutions is of considerable importance in its bearing upon the sensitiveness of the method. Among the galvanometers available for use with the bridge, that which seemed best suited for the work, was one having a resistance of about 10,000 ohms. It was therefore desirable to have the resistance to be tested as near to this value as other conditions would permit. On the other hand, the layer of liquid tested should be so thin that it can be excited to strong fluorescence throughout its thickness. Although we did not find it possible to satisfy both of these conditions, they were approximately met by the form of cell shown in diagram in Fig. 28.

[1] In the experiments of Cunningham and Regner the solvent was water.

The figure shows both a perspective view and a horizontal section of the cell. A thick piece of plate-glass, G, was cut of such a size as nearly to fill the cell and was held in position, tightly pressed against the two electrodes a, b (of platinum foil), by the corks C, C. Although the drawing is in other respects approximately to scale and nearly actual size, the thickness of the electrodes a, b is greatly exaggerated. The thickness of the layer of liquid between G and the walls of the tube was determined by the thickness of the electrodes and was about 0.1 mm. In the section shown in Fig. 28 the portions occupied by the solution are left unshaded. The length of the electrodes was about 20 mm. and their distance apart 2 mm.

The fluorescent substances tested were eosin, fluorescein, rhodamin, napthalin roth, and cyanin. As already stated, the solvent was in all cases absolute alcohol. The solutions were made quite concentrated, so that fluorescence was confined to a thin layer at the surface. The concentration was so adjusted as to make this fluorescent layer approximateiy 0.1 mm. thick.

The cell containing the solution to be tested was made one arm (C) of a bridge. The resistance of the arm M in series with C was in all cases 9,000 ohms, while the resistance of the third arm, R, was 5,000 ohms. The fourth arm, N, was varied until an approximate balance was obtained[1] and the apparent resistance was computed by the formula $C = MR/N$. Current was furnished by two gravity cells in series.

Polarization in the fluorescent solution made it impossible to obtain the true resistance by this method, and the apparent resistance of the cell (computed as if polarization were absent), is doubtless in error by 50 per cent. or more. But the sensitiveness of the arrangement to changes in the resistance of the test cell was high. In order to avoid disturbances due to variations in the polarization E.M.F. it was found necessary to keep both the battery circuit and the galvanometer circuit closed. Even the small change made in N during the adjustment of the balance produced a considerable alteration in the polarization, so that the adjustment often had to be continued for an hour or more before the needle of the galvanom-

[1] These resistances were chosen not because they gave the highest attainable sensitiveness, but because they were the most suitable ones that were available at the time.

eter was sufficiently steady for observations to be begun. During this time the cell was protected from the action of light by an opaque screen. When the conditions had become steady, or more frequently when the motion of the galvanometer needle was reduced to a slow uniform drift, the screen was removed and light from an arc was allowed to fall on the cell. After the effect of illumination had been noted, and when the needle had again settled down to a steady drift, the screen was replaced, and the throw of the needle in the opposite direction was observed.

In the measurement of so small an effect as that here considered it is clear that the heating effect of the rays from an arc is likely to produce serious errors, for the change in conductivity due to rise in temperature is unfortunately in the same direction as the change that we are attempting to detect. For this reason the use of the direct rays of the arc, even at the distance of a meter, was entirely out of the question. Even when a water cell was interposed in the path of the rays the needle was displaced through several hundred divisions. That this movement of the needle was due to rise in temperature, and not to the effect sought, was indicated by the fact that the change persisted after the rays were cut off; it was necessary to wait at least fifteen minutes before the original balance was approximately restored.

In order to avoid the disturbances due to rise in temperature we adopted the plan of dispersing the rays from the arc by a prism and using only those portions of the spectrum that were most effective in producing fluorescence. With this arrangement the effects observed were much smaller than before, but they were entirely free from any indication of temperature changes. Upon removing the screen, so as to illuminate that part of the fluorescent solution lying between the electrodes, a throw of the galvanometer needle was observed, and if originally free from drift the needle vibrated about a new position and finally came to rest. Continued illumination of the solution produced no increase in the deflection. Upon replacing the screen a throw in the opposite direction occurred, and the needle finally returned to its original reading. If observations were made while the needle was in motion, these throws were simply superposed upon the steady drift. In this case the effect of illumination was measured by the average of the two throws.

So far as we were able to judge, the effect produced by light reached its full value at once and ceased as soon as the light was cut off. The disturbance of the balance of the bridge was always such as to indicate an increase in the conductivity of the fluorescent solution. Upon repeating the experiments with rays from different portions of the spectrum it was found that a change in conductivity was produced only by those rays which were able to excite fluorescence in the solution tested. And so far as we could estimate the intensity of fluorescence by the eye, the rays which gave the most intense fluorescence also produced the greatest change in conductivity. In the case of eosin we were able to follow both effects to the extreme edge of the violet, while illumination by the red of the spectrum produced no effect.

In order to form an estimate of the magnitude of the change produced we observed in each case the throw caused by increasing or decreasing the resistance N by one ohm. By comparing this with the throw due to illumination, it was possible to express the observed change as a fraction of the normal (apparent) resistance. The results are given in Table III. The light used to illuminate the solution, in the case of the measurements included in the table, was that which produced the brightest fluorescence.

We have also tested in the same way one solution that was not fluorescent, namely, an alcoholic solution of fuchsin. The result was entirely negative. No change in resistance due to illumination

TABLE III.

Increase in Electrical Conductivity due to Fluorescence.

Substance.	N	Apparent Resistance of Solution.	Throw Produced by Illumination.	Throw Produced by Increasing N by 1 Ohm.	Increase in Conductivity Due to Illumination.
Eosin.	155	300,000	57 mm.	33 mm.	1.1%
Napthalin roth.	45	1,000,000	1	39	0.05
Fluorescein.	300	150,000	10	30	0.11
Rhodamin.	360	125,000	20	40	0.14
Cyanin.	170	270,000	40	45	0.52

could be found in any part of the spectrum, although the sensitiveness of the bridge was such that a change of .008 per cent. could have been detected. The solution was an old one and had prob-

ably been made with commercial alcohol, since the resistance, 90,000 ohms, was much lower than that of the other solutions. For this reason we are not inclined to look upon this single experiment with a non-fluorescent solution as possessing much significance.

In the preceding description of the experiments upon fluorescent solutions we have ascribed the observed movements of the galvanometer needle to a change in the *resistance* of the solution. The galvanometer deflections undoubtedly indicate a disturbance in the balance of the bridge; but this disturbance might equally well result from a diminution in the E.M.F. of polarization. Without special modifications the method does not permit a separation of these two possible effects. In the case of eosin special experiments were made bearing upon this point; but with the other solutions we have no direct evidence to show that the observed change is not due to the influence of light upon the polarization of the cell.

The experiments referred to in the case of eosin were of two kinds. In the first of these a bridge method was employed as before. The solution was contained in a glass tube originally about 5 mm. in diameter. A portion of this tube had been drawn down to a diameter of about 1 mm. and the current passed through the liquid contained in this contracted part. The platinum electrodes were placed in the larger part of the tube at each end. We were thus able (1) to illuminate the solution about either electrode while the remainder of the tube remained dark; or, (2) to illuminate the contracted part of the tube while screening the electrodes. In the latter case the effect was observed, as in the experiments already described. In the former case only a very small change could be detected. Although this arrangement was less sensitive than that in which the cell shown in Fig. 28 was used, the results show that only a small part of the effect previously observed can be attributed to a change in polarization.

The other experiments with eosin that bear upon the question of polarization were of an entirely different character, and represent one of our many early attempts to devise a satisfactory method of attacking the general problem. Fig. 29 shows both the form of tube used to contain the solution and a diagram of the connections. The

platinum wire electrodes *a*, *b* were connected to the terminals of the secondary of an induction coil, *I*, and to the two pairs of quadrants of an electrometer, *E*. The electrode *C* at the center of the tube was connected to the needle. The primary of the induction coil was excited by an alternating current of 120 cycles. When the solution was not illuminated the electrometer needle stood nearly at its zero. Under these circumstances illumination of the upper half of the tube produced a deflection in one direction, while the illumination of the lower half gave an approximately equal deflection in the opposite direction. The direction of the deflection in each case was such as to indicate a decrease of resistance. The spectrum of the arc was used in these experiments as in those made by the

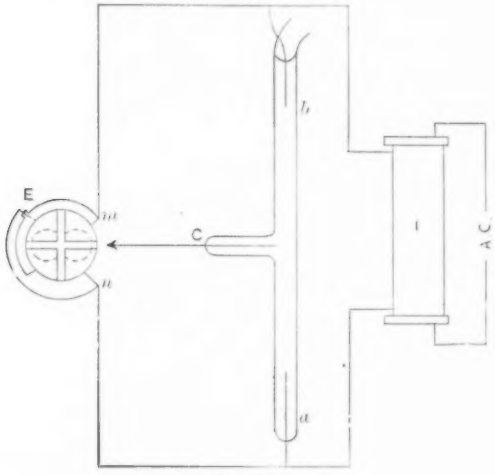


Fig. 29.

bridge method; and the evidence that the effect was due to fluorescence, and not to rise of temperature, was as conclusive as in the experiments already described. The method was less sensitive, however, and was therefore used only in the case of eosin.

The results of these two widely different methods are conclusive in showing that in the case of eosin we have to deal with a change in conductivity rather than a change in polarization. That this statement is equally true in the case of the other solutions tested appears probable.

RADIATION PYROMETRY.[1]

BY C. W. WAIDNER AND G. K. BURGESS.

IN a study of some special problems in the measurement of high temperatures we have been lead to examine, in some detail, the field of radiation pyrometry, which is the line along which the most marked advances in temperature measurement have been made in recent years, and have made a study of the sources of error, necessary precautions, and limits of attainable accuracy in the use of some of the best types of radiation pyrometers that are at present available to the experimentalist, and have applied these pyrometers to the investigation of several problems that are of interest in this field of temperature measurement.

GENERAL DISCUSSION OF RADIATION PYROMETRY.

Under the term radiation pyrometry may be grouped all those methods in which the temperature of bodies is estimated from the radiant energy emitted, either in the form of visible light radiation or of the longer infra red waves that are studied by their thermal effects. The obvious advantages and special field of application of this system of pyrometry are, in the measurement of the temperatures of inaccessible or moving objects, the estimation of temperatures far beyond the range of any pyrometer requiring contact with the heated substance, and the rapid examination of surfaces for uniformity of heating, a problem of great importance in metallurgical processes.

A great advantage of optical pyrometry is the rapid variation in the photometric intensity of light with variation in temperature. Thus, for example, if the intensity of the red light, $\lambda = 0.656\,\mu$, emitted by a body at 1,000° C. is called 1, at 1,500° C. the intensity will be over 130, and at 2,000° C. over 2,100. Further, for the total luminous intensity of the light emitted by platinum, Lummer

[1] Communication from the National Bureau of Standards.

and Pringsheim[1] have found that at 900°, 1,400°, and 1,900°, abs., respectively, the light increases 30, 18 and 14 times as rapidly as the temperature. It is this fact alone, of the rapid change in intensity of light with change in temperature, that makes it possible for the trained eye to estimate the approximate temperature in the many industrial processes dependent on temperature control.

It would therefore appear that a system of pyrometry based on the intensity of the light emitted by incandescent bodies would be an ideal one, inasmuch as a comparatively rough measurement of the photometric intensity would fix the temperature quite accurately. This, however, is only partly true; it is limited somewhat by the fact that different bodies, although at the same temperature, emit vastly different amounts of light. Thus, the intensity of the radiation from incandescent iron or carbon at 1,000° C., for example, is many times greater than that emitted by such substances as magnesia or polished platinum at the same temperature. Consequently, if any conclusions were drawn as to the temperatures of these bodies from the light that they emit, it might lead to large errors. Thus, at 1,500° C. this difference in the intensity of the light emitted by carbon and by polished platinum would lead to a difference in the estimated temperatures of these bodies of about 90° C., and less at lower temperatures.

The possible erroneous conclusions that might be drawn from such a system of optical pyrometry is still further emphasized in considering the results to which it would lead if applied to the measurement of the temperature of flames. Here the intensity of the light would vary with the thickness of the flame in the line of sight. If applied to the estimation of the temperature of a colorless Bunsen flame the method would entirely fail.

At first sight the difficulties here enumerated, incident to the different emissivities of bodies, being a function not of the temperature alone, but dependent on other properties, such as conditions of surface and materials entering into composition, might seem insurmountable, and sufficient to condemn the use of optical pyrometry. Such, however, is fortunately not the case. It is, therefore, necessary to consider briefly the principles on which optical pyrometry

[1] Lummer and Pringsheim, Verh. d. Deutsch. Phys. Ges., 11, p. 89, 1900.

is based, its limitations, advantages, and the necessary precautions that must be observed in overcoming these difficulties.

Kirchoff[1] in one of the most important contributions to the theory of radiation, was led to the important conception of what he termed a "black body," which he defined as one which would absorb all radiations falling on it, and would neither reflect nor transmit any. He further pointed out the important fact that the *radiation from a black body was a function of the temperature alone*, and was identical with the radiation inside an enclosure all parts of which have the same temperature. The first experimental realization of a black body as a practical laboratory apparatus was made by Wien and Lummer,[2] by heating the walls of a hollow opaque enclosure as uniformly as possible and observing the radiation coming from the inside through a very small opening in the walls of the enclosure. It is evident that such a body will absorb practically all the radiation incident through the small opening, and this whatever the material of the walls, for unless the walls were totally reflecting, all the radiation will be absorbed except that portion which might again escape through the opening; the presence of the opening, therefore, causes a slight departure from ideal black body conditions.

Black body radiation in the interval 600° to 1,600° C., may be most conveniently obtained in the laboratory by the electrically heated black body devised by Lummer and Kurlbaum,[3] which consists of a porcelain or fire-clay tube, suitably protected by surrounding tubes and air jackets, which is wound with a platinum foil heating coil, and whose temperature can be maintained constant for long intervals by suitable regulation of the electric heating current. The radiation coming out of the end of this tube from an object at the uniformly heated region near the center, in contact with a thermo-couple, is a very close approximation to ideal black body radiation at a known temperature.

No body is known whose surface radiation is exactly that of a black body. The radiation from carbon and iron approximates fairly near to black body radiation, while the radiation from polished platinum and the white oxides departs very far from it.

[1] Kirchoff, Pogg. Ann. **109**, p. 275, 1860.

[2] Wien and Lummer, Wied. Ann., **56**, p. 451, 1895.

[3] Lummer and Kurlbaum, Verh. d. Deutsch. Phys. Ges., **17**, p. 106, 1898; Ann. d. Phys., **5**, p. 829, 1901.

Radiation pyrometers are calibrated in terms of the radiation from a black body, as this radiation alone is a function of the temperature only. They will then give true temperatures only when used on black bodies. When used to measure the temperature of other bodies ther adiation pyrometer calibrated in this way will not give the true temperature but the equivalent *black body temperature, i. e.*, the temperature a black body must have to send out radiation of the same intensity and of the same kind. Two bodies having the same black body temperature may differ very considerably in their true temperatures, thus in the illustration already cited for carbon and platinum at 1,500° C., the difference is of the order of 90°. The temperature of a piece of platinum at 1,500° C. (as measured by a thermo-couple), will, if measured by an optical pyrometer using red light, appear to be about 1,365° C., and if green and blue light are used in the photometry, about 1,405° and 1,425°, respectively (see p. 443), showing that platinum approximates more nearly to black body radiation for green and blue, than for red light.

The great objection to the use of radiation pyrometers, that their indications are not dependent on the temperature alone but also on the widely varying emissivities of different bodies, may then be answered as follows. These pyrometers can be used to measure the equivalent black body temperatures, and it is then possible to pass over to true temperatures by means of such experiments as those given on p. 446, giving the departure from black body radiation. Further, in many cases arising in industrial operations requiring the use of a pyrometer, the body whose temperature is to be measured is not out in the open but is found enclosed in a furnace whose walls are at a temperature not far different from that of the body, so that the radiation is a fair approximation to black body radiation, and the indications of the radiation pyrometer will not differ much from true temperatures. In many other cases, *e. g.*, when the problem at hand is the measurement of the temperature of an enclosed furnace or of a fused metal bath, the difficulty may be overcome by immersing in the bath or furnace a closed end porcelain or iron tube, and observing the radiation coming out of the open end of this tube, in which case the indications of the radiation pyrometer will give true temperatures.

Often a knowledge of the black body temperature fulfills every requirement of the problem at hand, whether it be the control of temperature in an industrial operation or a scientific experiment, and this a radiation pyrometer gives with a very satisfactory precision.

The temperature of any body as measured by a radiation pyrometer will in general (luminescence effects excluded) be lower than its true temperature. There is a source of error, however, that may act in the direction of making the pyrometer read too high, namely, due to light reflected by the body whose temperature is being measured, coming from surrounding flames and hotter objects. Experiments bearing on this point, and methods of eliminating this source of error are discussed under "Diffuse and Reflected Light."

METHODS OF RADIATION PYROMETRY.

The methods of radiation pyrometry that are available for the estimation of high temperatures, and which have been carefully studied by a number of investigators, may be broadly grouped under the following heads:

1. *Color Estimation.* — The estimation of the temperature of bodies by the color of the emitted light is still the most widely used, unfortunately so, of all pyrometric methods, especially in metallurgical operations. A comparison by Howe[1] of his results with those of White and Taylor shows that even with skilled observers, estimates by the unaided eye may differ by 50° C. or more at 800° C., and by much greater amounts at higher temperatures.

2. *Photometric and Spectrobolometric Methods.* — Becquerel was among the first to suggest the measurement of the temperature of incandescent bodies by photometric measurement of the intensity of the light emitted. As this method is now generally applied, it consists of a photometric comparison of the red light emitted by the body under observation with the red light emitted by a standard comparison source (gasoline or electric). Red light is chosen because it enables the range of measurement to be extended to the lowest temperatures measurable optically. The first practical form of optical pyrometer utilizing this principle was brought out by Le Chatelier. This instrument, together with those brought out

[1] Howe, Eng and Min. J., 69, p. 75. 1900.

more recently by Wanner, Féry, Holborn and Kurlbaum, and Morse will be briefly discussed later with a view to their trustworthiness as instruments of precision.

The use of monochromatic light obviates the difficulties incident to the photometry of lights of different color, and further it makes it possible to utilize in the calibration of these instruments Wien's law for the distribution of energy in the spectrum of a black body,

$$J = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}}$$

where J is the intensity of the light of wave-length λ, T is the absolute temperature, e the base of the natural system of logarithms. and c_1 and c_2 constants.

This may be written :

$$\log J = K_1 + K_2 \cdot \frac{1}{T}$$

$$\text{where } K_1 = \log c_1 - 5 \log \lambda \text{ and } K_2 = c_2 \frac{\log e}{\lambda}.$$

If working with visible radiation it therefore requires only two photometric measurements at two known absolute temperatures to completely standardize a pyrometer. For infra-red monochromatic radiation a dispersing apparatus (non-absorbing) must be used in connection with a bolometer, thermopile, or other instrument for detecting radiation. For long wave-lengths and high temperatures, Wien's equation ceases to hold and use must be made of Planck's equation

$$J = c_1 \lambda^{-5} \left(e^{\frac{c_2}{\lambda T}} - 1 \right)^{-1}$$

which the researches of Lummer and Pringsheim,[1] Paschen,[2] and Rubens and Kurlbaum[3] have shown satisfies the experiments for black body radiation throughout the widest range of measurable temperatures (— 200° C. to + 1,500° C.), and wave-lengths (to $\lambda = 51.2\ \mu$). For the wave-lengths of the visible spectrum, however, Wien's equation represents the results of experiment with every required degree of precision, for as Lummer and Pringsheim

[1] Lummer and Pringsheim, Verh. d. Deutsch. Phys. Ges., 3, p. 42, 1901.
[2] Paschen, Ann. d. Phys. 4, p. 277, 1901.
[3] Rubens and Kuribaum, Ann. d. Phys., 4, p. 649, 1901.

have pointed out, for values of λT not exceeding 3,000, Wien's and Planck's equations differ by less than 1 per cent. The former may, therefore, under these conditions be used for extrapolation to the highest attainable temperatures (4,000° or more).

3. *Ratio of the Intensities of Two Wave-lengths.* — Crova[1] in 1878 devised a method based on the relative variation in the intensity of two different monochromatic radiations, red and green, but as Violle has shown, the ratio of intensities $\lambda = 0.656\ \mu$ (red) and $\lambda = 0.482\ \mu$ (blue) varies only in the ratio 1 to 4.5 over a temperature interval of 700° C., and again the lower limit of temperature determinations is given by the green (about 1,200°) so that Crova cannot be said to have made use of a practicable principle, although he actually used his spectrophotometer in some of his researches.

4. *Upper Limit of Spectrum.* — Another method, also suggested by Crova, susceptible of use at lower temperatures, was based on the use of the upper limit of the spectrum of an incandescent body. Hempel[2] has made the most extensive investigation of the possibilities of this method, using a special form of spectroscope and luminescent screen for observing when the upper limit of the spectrum is beyond the visible radiations, but compared with other photometric and radiation pyrometers only crude results can be obtained.

5. *Maximum Energy in Spectrum.* — (*a*) Displacement of λ_m. In this method use is made of the displacement, with temperature, of λ_m, the wave-length having maximum energy, as given by Wien's displacement law

$$\lambda_m T = \text{const.} \equiv A$$

or (*b*) by the maximum-energy law,

$$E_{\max} T^{-5} = \text{const.} \equiv B.$$

The constant A varies from 2,930 for a black body to 2,630 for polished platinum. A bolometer, thermopile or other instrument for detecting radiation is used in connection with a dispersing apparatus (non-absorbing) to locate λ_m or to measure $E_{\max}$. If the value of the constant is known for the particular radiating substance

[1] Crova, J. de Phys., **7**, p. 357, 1878; **9**, p. 196, 1879. Ann. de Chem. et Phys. (5), **19**, p. 472, 1880.

[2] Hempel, Angewandte Chem., **14**, p. 237, 1901.

the absolute temperature can then be computed. As the black body is the best radiator and polished platinum is one of the worst, it follows that if λ_m is known, the limiting temperatures between which the true temperature of the body must be found, if its radiation is purely thermodynamic and intermediate between that of a black body and polished platinum, are given by

$$T_{\max} = \frac{2{,}930}{\lambda_m} \text{ and } T_{\min} = \frac{2{,}630}{\lambda_m}.$$

Lummer and Pringsheim[1] have used this method to estimate the limiting temperatures of a number of radiants, such as the electric arc, incandescent and Nernst filaments, and others.

The displacement law is among the best established of the radiation laws, both from the theoretical and experimental side, so that this method is of considerable theoretical interest; yet it is not capable of a high degree of precision on account of the difficulty of locating λ_m, due to the flattened form of the energy curve.

6. *Energy of Total Radiation.* — Assuming the Stefan-Boltzmann law, $E = K(T^4 - T_0^4)$ as established, where E is the energy of total radiation, visible and invisible, T the absolute temperature of the radiating black body source, T_0 that of the receiving instrument, and K a constant, this method can be used to measure temperatures of bodies even long before they become incandescent.

For this purpose such instruments as the bolometer of Langley, Crooke's radiometer as modified by Rubens and Nichols, the actinometers of Pouillet and Violle, the radiomicrometer of Boys, and the thermopile may be used.

Féry has recently brought out a practical form of instrument, called a thermoelectric telescope (see page 439), based on the energy of total radiation, which is measured by the rise in temperature produced at one junction of a very sensitive thermo-couple joined to a direct reading pyrometer galvanometer.

7. *Berthelot Interference Method.* — D. Berthelot[2] has introduced a new system of gas thermometry, based on the relation between index of refraction, temperature, and density of a gas. For this purpose a beam of light is divided into two parts, one going through

[1] Lummer and Pringsheim, Verh. d. Deutsch. Phys. Ges., **4**, p. 36, 1901.

[2] Berthelot, Ann. de Chim. et de Phys. (7), **26**, p. 58, 1902.

the heated gas contained in a refractory tube, which can be kept at a high temperature by a heating coil (or by a current through the body of the tube itself) and the other through a tube of the same gas whose density can be conveniently varied; the two beams are then brought together and produce interference bands. The pressure in the cold tube is varied to prevent a shift of these bands. This is not a radiation method, but may later form an independent check on the extension of the radiation laws to very high temperatures.

STUDY OF INSTRUMENTS.

The radiation pyrometers which have come into use may be classed according to the law in terms of which their indications are given. Those based on Wien's law are the Le Chatelier,[1] and Féry's modification, known as the absorption pyrometer,[2] and the Wanner polarizing photometer.[3] Féry's thermo-electric telescope,[4] with fluorite lens is calibrated in terms of the Stefan-Boltzmann law, while the Holborn-Kurlbaum[5] and Morse[6] instruments require an empirical calibration.

All but Féry's thermo-electric telescope are photometers, the first three employing two red fields side by side, one given by a standard light and the other by the object studied, and the last two making use of an incandescent lamp filament disappearing against the object observed.

Le Chatelier's Pyrometer. — This instrument is shown in Fig. 1, in which L is a gasolene lamp the intensity of whose light, as viewed through a red glass after reflection from the mirror M, serves as a comparison standard for the light from the object studied, which passes through the iris-diaphragm D, whose aperture is adjusted until the photometric fields are of the same brightness.

Féry has replaced the iris diaphragm by a variable absorbing wedge, thereby decreasing somewhat the lower temperature limit and the sensibility of the instrument. He has improved it by

[1] Le Chatelier, C. R., 114, p. 214, 270, 1892; J. de Phys. (3), 1, p. 185, 1902.
[2] Féry, J. de Phys. (4), 3, p. 32, 1904.
[3] Wanner, Phys. Z. S., 3, p. 112, 1902.
[4] Féry, C. R., 134, p. 977, 1902.
[5] Holborn and Kurlbaum, Ann. d. Phys., 10, p. 225, 1902.
[6] Morse, U. S. Letters Patent, 696,878; 696,196, 1902.

rendering it movable about any axis, by the use of an aperture of constant angle which renders the indications independent of the focussing, and by employing a 45° mirror silvered so as to give a field as shown at *C* when looking at a crucible. The original Le Chatelier pyrometer may also be improved by substituting an electric lamp and diffusing screen for the gasolene comparison lamp.

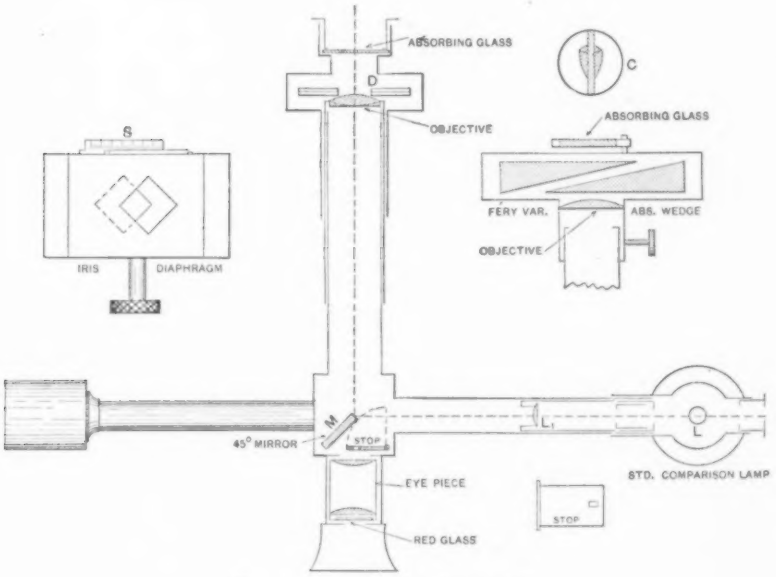


Fig. 1. Le Chatelier Pyrometer.

Le Chatelier calibrated his instrument in terms of the empirical formula

$$J = 10^{a} T^{-\frac{b}{T}} \tag{1}$$

where a and b are constants depending on the unit of intensity, and J, the intensity, is given in terms of the square of the scale readings. A more simple calibration is made in terms of Wien's law, in the form

$$\log J = K_1 + K_2 \cdot 1/T. \tag{2}$$

A good monochromatic glass (such as Jena No. 2745) is required if any calibration is to be relied on at very high temperatures. The following table shows the results of a calibration by both methods.

Observed Temperature (Absolute).	Temperature Calculated by Le Chatelier Formula.	(Le Chatelier) $t_{obs.}-t_{calc.}$	Temperature Calculated by Wien Formula.	(Wien) $t_{obs.}-t_{calc.}$
975°	975°	0	982°	− 7
995	994	+ 1	1,001	− 6
1,147	1,147	0	1,150	− 3
1,154	1,148	+ 6	1,150	+ 4
1,191	1,190	+ 1	1,189	+ 2
1,211	1,214	− 3	1,213	− 2
1,278	1,276	+ 2	1,274	+ 4
1,296	1,290	+ 6	1,287	+ 9
1,398	1,400	− 2	1,396	+ 2
1,459	1,464	− 5	1,460	− 1
1,587	1,602	−15	1,597	−10

The central portion of the flame of a Hefner standard was used as the unit of intensity, the data satisfy the following equations[1]

$$\log J = 6.697 - 9{,}983\,\frac{1}{T} \qquad \text{(Wien's Eq.)}$$

$$J = 10^{7.77}\,T^{-\frac{3660}{T}} \qquad \text{(Le Chatelier's Eq.)}$$

The calibration was carried out by sighting the pyrometer upon the bottom of a small fire-clay crucible placed at the center of a nickel wound electric furnace 60 cm. long and 2 cm. opening; temperatures were measured by two thermocouples with junctions in contact with the crucible.

The effective wave-length of the red light transmitted by the glass used before the eye piece was determined as 0.64 μ. As shown on p. 427 the value of K_2 in the Wien equation is given by

$$K_2 = \frac{c_2 \log_{10} e}{\lambda} = 9{,}983$$

$$\therefore c_2 = 14{,}700.$$

This would indicate that the radiation from the interior of the electric furnace used in this work is a close approximation to black body radiation, the constant c_2 for which is about 14,500. Covering with iron oxide the radiating fire-clay surface found at the center

[1] In the computation of the constants of the equations, the observations found in the table have not all equal weight.

of the furnace produced no very appreciable increase in the "blackness" of the radiation (not greater than 5° or 10°).

The gasolene comparison lamp is most satisfactory when not used where there are drafts; also the wick does not char. As only a small area of the flame is used, changes in height of the flame have but a small influence on the indications; thus we have found a variation in height of 2 mm. is equivalent to a temperature change of less than 6° at 1,000° C. The flame may be easily set to a few tenths of a mm., by inserting in the lamp holder a sight similar to that on the Hefner. The effect of time of burning on the constancy of the lamp is also small, as shown by the following observations.

	Cat's Eye Reading.	Δ in Per Cent.	Δ in Degrees C.
After 25 minutes' burning.	26.03	1.7	0.9° C.
" 45 " "	26.26	7.5	4.2
" 2 hours' "	27.03	5.0	2.7
" 2¾ " "	26.68		

Varying samples of gasolene gave results indistinguishable from each other, and even diluted to over 20 per cent. with a pure, heavy kerosene of flash point = 135° C., identical readings were still obtained.

The instrument may readily be focussed to 2 mm., corresponding to a temperature change of 1° at 1,000°, so that if the focussing is correct to 5 mm., a sufficient precision will be obtained. Varying by a fourth of its value the distance of the pyrometer without refocussing, as in rapid work, will introduce an error of only 5° at 1,000° C.

The agreement among different observers in taking readings is

	Without Absorption Glass.				With Absorption Glass.	
Observer.	1	2	3	4	1	3
Cat's eye scale reading.	7.4	7.8	7.6	7.3	25.7	25.8
	7.4	7.9	7.8	7.0	24.0	24.8
	7.2	7.7	7.6	8.0	23.6	26.0
	7.8	7.8	7.7	7.1	24.1	25.8
	7.7	7.7	7.8	8.3	25.4	24.8
	7.8	7.7	7.4	8.0	24.8	24.9
					24.8	25.3
Means.	7.55	7.73	7.65	7.60	24.63	25.34

illustrated by the following observations on the determination of the coefficient of absorption of an absorbing glass placed before the objective.

Observers 2 and 4 had no previous experience with the instrument. The values of K computed from the results of observers 1 and 3 differ by 3 per cent., corresponding to a difference in temperature of less than 2° at 1,000°.

The above discussion shows the ordinary form of Le Chatelier pyrometer to possess a precision of about 1 per cent. from the lowest temperature (600° C.), which may be estimated optically.

Wanner Pyrometer. — In this instrument, Fig. 2, the monochro-

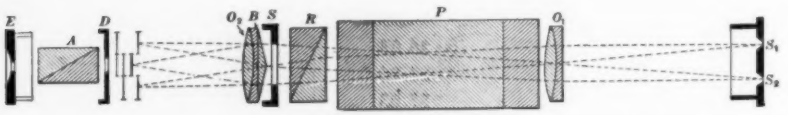


Fig. 2. Wanner Pyrometer.

matic red field is produced by a direct vision prism P and slit S. The slit S_1 is illuminated by a comparison electric lamp and S_2 by the source under investigation. Both beams are divided into components polarized at right angles by the Rochon prism R, and the biprism B is so cut as to bring but two of the eight images side by side in front of the opening D before the analyzer A. The analyzer is set at the normal point by adjusting the brightness of the electric lamp, varying its current or position, to equality with a Hefner placed in a definite position.

In terms of the circular scale attached to the analyzer, we have

$$\frac{J}{J_0}\tan^2\varphi$$

where J_0 is the intensity of light from the standard; Wien's law gives

$$\log_{10}\left(\frac{J}{J_0}\right) = \frac{C_2}{\lambda}\log_{10}e\left(\frac{1}{T_0}-\frac{1}{T}\right),$$

so that a knowledge of the scale reading when $J = J_0$, *i. e.*, at the normal point, and the black body temperature of the standard source

are all the data needed for calibration of the scale if it is correctly graduated.

The constancy of the Hefner as here used is shown by the following observations taken at different times when the current through the electric comparison lamp was kept constant:

Reading Wanner Scale.[1]	Deviations.
39.9	−0.28
39.9	−0.28
40.1	−0.48
39.9	−0.28
39.1	+0.52
39.2	+0.42
39.8	−0.18
39.0	+0.62
39.62	0.38

This shows that the flame is constant enough to reproduce the normal point to 0.5 per cent. in temperature, but this must be increased to about 1 per cent., due to the uncertainties in making a photometric setting. The electric lamp can be set at the normal

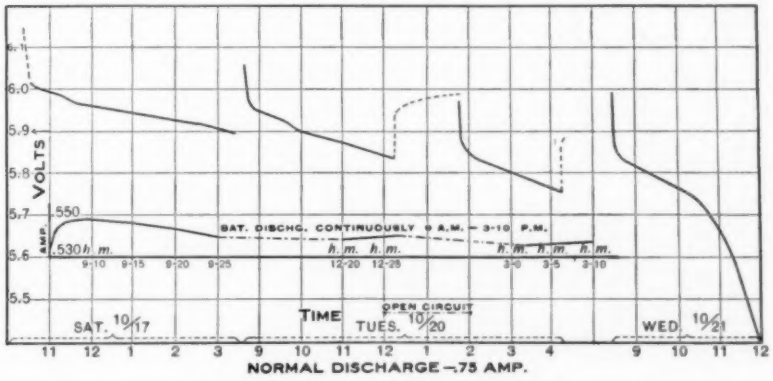


Fig. 3. Discharge Curve of Battery.

point to better than 1 per cent. if care is taken that the diffusing glass before the slits S_1 and S_2 is clean and is always inserted in the same position. The most serious source of error is due to lack of constancy in the electric lamp, due to variations in current from the storage battery, the percentage change in light being of the order

[1] 39.6 divs. on scale of Wanner pyrometer = 1,157° C.; at this part of the scale one div. = 6° C.

of six times the percentage change in current. In order to obtain a precision of 5° at 1,000° C., this current must be constant to 1 per cent., or, as our experiments have shown, to 0.006 amperes for the range 1,000° to1, 500° C. The accompanying table and plot shows the behavior of a three-cell battery of 10 ampere-hours' capacity furnished with the instrument:

Time.	Wanner Scale. Rdg.	Current Through Lamp.	Per Cent. Change in Current Through Lamp.	Apparent Change in Temperature Observed.
15 min.	31.2	0.5645	0.1	1° C.
20 "	31.8	0.5640	1.7	10
27 "	32.7	0.5550	4.3	25
37 "	34.6	0.5400		
38 "		disconnected battery two minutes.		
40 "	32.5	0.5570	1.5	7
42 "	31.7	0.5610	0.6	3
45 "	32.5	0.5560	2.5	15
47 "	33.1	0.5405	4.1	24

A 75 ampere-hour battery gave similar results. It is, therefore, evident that in work of precision it is necessary to control the current through the lamp by means of a rheostat and milliammeter, as

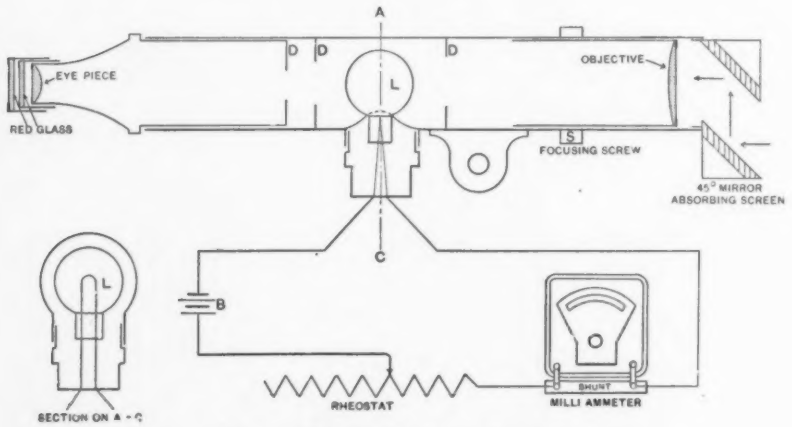


Fig. 4. Holborn-Kurlbaum Pyrometer.

otherwise errors of over 25° may be introduced, and greater ones with the battery in poor condition.

This pyrometer is difficult to sight on small objects, not being a

telescope, but on the other hand requires no focussing. Another limitation is due to the fact that the instrument is a polariscope, so that if the light is polarized considerable errors may be introduced in its indications. This effect is eliminated or proved absent by taking readings in four azimuths.

Used with the proper precautions, this pyrometer is one of great precision and convenience.

Holborn and Kurlbaum Pyrometer. — Fig. 4 shows the arrangement of this instrument; the tip of the filament *L* of the four volt incandescent lamp is set to the same brightness as the object whose temperature is sought, by means of a rheostat. When the filament

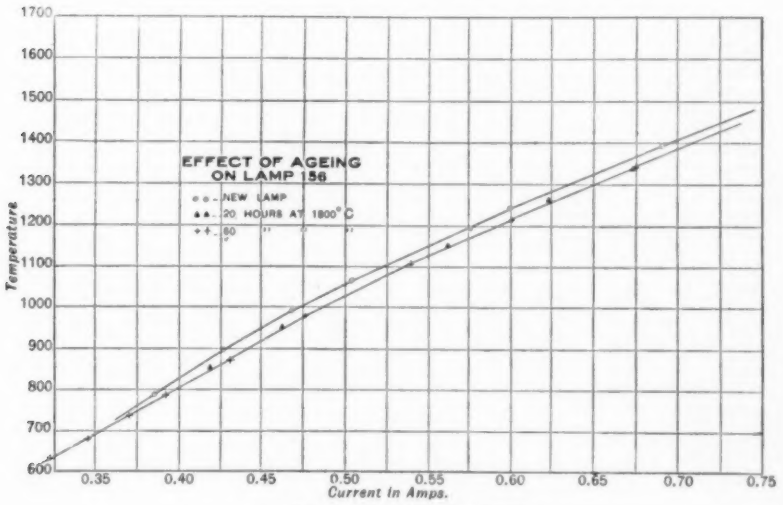


Fig. 5. Ageing of Lamps.

disappears against the bright background, the current through it is a measure of the temperature sought, when the lamp has been calibrated. One or more red glasses is placed before the eyepiece as the temperature rises above 900° C., and for extreme temperatures, above 1,500° C., absorbing glasses or mirrors are inserted in front of the objective.

The constancy of indications of this instrument is dependent upon the permanence of the lamp filaments used. Unaged lamps may change by over 25°, as shown by the accompanying plot, but when once aged for 20 hours at 1,800° C., these lamps will not change

appreciably in several hundred hours if not heated above 1,500° C. The relation between current and temperature is well given by the quadratic

$$C = a + bt + ct^2$$

where the coefficient c is very small, so that for short ranges of temperature the relation may be taken as linear. A separate calibration is required for each lamp.

The sensibility of this instrument is shown by the following set of observations:

Temperature from H-K Pyrometer.	Temperature from Thermo-couple.	Temperature from H-K Pyrometer.	Temperature from Thermo-couple.
1,347° C.	1,347° C.	632° C.	634° C.
1,351	1,347	634	633
1,343	1,343	633	633
1,338	1,342	633	632
1,342	1,342		

For use at extreme temperatures the absorption factor K of the absorbing glasses used may be calculated from Wien's equation:

$$\log_{10} K = \log_{10}\left(\frac{J_1}{J_2}\right) = \frac{c_2}{\lambda}\log_{10} e\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where T_1 and T_2 are the apparent black body temperatures (absolute) given by the pyrometer, when sighting on a constant source of radiation first without and then with the absorbing medium. This method of determining K, as well as using Wien's equation in the above form for the estimation of extreme temperatures is applicable also to the other optical pyrometers.

Morse Pyrometer. — This instrument is the same in principle as the preceding, but there is no focussing device provided and the range is limited to that attainable with the unaided eye. A large spiral lamp is used, requiring a more costly battery installation, and it is quite fatiguing to match a particular spot of this spiral with the background. In spite of its crude form, this pyrometer is capable of a precision of better than 5° C. in the limited range for which it is adapted.

Féry Thermo-Electric Telescope. — Radiation from the source whose temperature is sought is focussed by fluorite lens, F (Fig.

6), on one function of a minute iron-constantan couple in series with a potential galvanometer, whose deflections are proportional to the energ yreceived by the couple, and hence to the fourth power of the absolute temperature, according to the Stefan-Boltzmann law, if the radiating source is a black body.

This relation is only true on the condition that fluorite has a constant coefficient of absorption for all wave-lengths. At low temper-

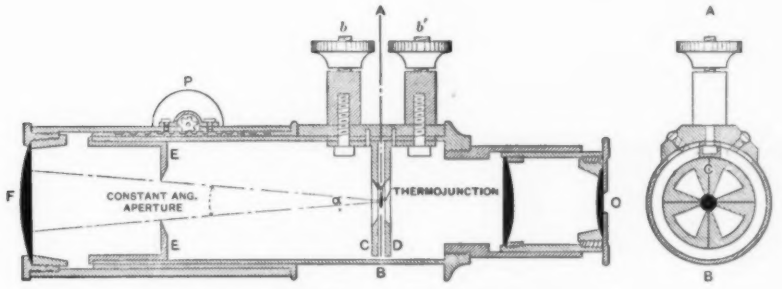


Fig. 6. Féry Thermo-Electric Telescope.

atures a large proportion of the energy exists in the form of long wave-lengths, and as fluorite has an absorption band in the infra red (near 6μ) the Stefan-Boltzmann law will not hold for this region. Above 900° C., however, Féry has found this instrument to give results to better than one per cent. In making a temperature measurement it is necessary to focus the image of the incandescent body upon the thermo-junction by means of the eyepiece *O* and this image must completely cover the junction.

A glass objective may replace the fluorite, when an empirical calibration becomes necessary.

This pyrometer, since its indications are given by a pointer over a scale, is readily made recording, a desideratum in many pyrometric investigations.

Comparison of Various Types of Radiation Pyrometer.

An experimental study of the behavior of the various radiation pyrometers shows that no one instrument can claim a decided superiority as to precision, certainty and ease of calibration, permanence of indications, and range. All of the instruments mentioned

above are capable of an accuracy of one per cent. in temperature measurement in the ranges for which they are adapted for use, although this accuracy is not attained with the same ease in all cases. With the Wanner pyrometer, for instance, a rheostat and milliammeter have to be inserted in the lamp circuit; and with the Holborn-Kurlbaum and Morse pyrometers, although this accuracy is readily secured, the constancy of the lamp must be assured.

It is possible to control a given temperature or measure temperature differences much more exactly than reproduce absolutely any temperature. For relative temperature measurements the precision attainable is better than one per cent., except possibly for the Féry absorption pyrometer, and may be even as good as 2° at 1,500° C., with the Holborn-Kurlbaum pyrometer.

The lowest temperature measurable optically is about 600° C., which may be reached with the Le Chatelier, Holborn-Kurlbaum and Morse instruments. The Wanner pyrometer and the Féry thermo-electric telescope cannot be used below 900° C.

Regarding the upper limit, there is none except for the Morse, which is difficult to use above 1,100° C.; but for very high temperatures, above 1,500° C., where they can only be determined by extrapolation in terms of some radiation law, the most reliable results will be given by those pyrometers obeying one of these laws the most exactly. Thus, instruments calibrated in terms of Wien's law, but making use of a red glass which is not sufficiently monochromatic, the Le Chatelier, the Féry absorption, and also the Holborn-Kurlbaum pyrometer in the region for which the absorption mirrors or glasses have to be used, will depart from the true temperature scale more than the Wanner pyrometer, which using strictly monochromatic light will obey Wien's law, if its reading circle is correctly graduated and set. The Féry thermo-electric telescope with fluorite lens should agree with the photometric pyrometers, as Wien's and Stefan's laws have been found experimentally in accord to at least 2,000° C., and they probably agree up to the temperature of the arc (3,600° C.).

For the calibration of all these pyrometers, the Holborn-Kurlbaum and Morse excepted, two known temperatures are sufficient; while for the latter a considerable number of points is necessary except for use over a small range.

The only instrument which could readily be made recording is the Féry thermo-electric telescope.

Special Problems in Optical Pyrometry.

Departure from Black Body Radiation. — Inasmuch as optical pyrometers are calibrated in terms of the radiation emitted by a black body, the temperature as determined by them will depend, as we have seen, on the nature of the incandescent body observed. It is, therefore, of interest to determine the amount by which such indications differ from the true temperatures. With this object in view we have determined the *black-body temperatures* of a number of substances at well-known temperatures, as given by the melting points of pure metals and salts.

Radiation from Platinum. — Among the substances studied was polished platinum, because it deviates farthest from a black body, and thus gives an idea of the maximum difference to be expected. In these experiments for determinations up to 1,500° C. use was made of a Joly meldometer[1] and a Holborn-Kurlbaum optical pyrometer. For experiments at the melting point of platinum a platinum strip about 5 cm. long and 4 mm. wide was cut narrow at the center so that the optical pyrometer could be focussed on the exact spot at which the strip melted. The electric current through the strip was slowly raised until the strip fused, and the reading of the optical pyrometer at this instant gives the black body temperature corresponding to the melting point of platinum (1,780° C.) for the particular color of light used. The results of these experiments are given in the following table: For red ($\lambda = 0.651\,\mu$), green ($\lambda = 0.550\,\mu$), and blue ($\lambda = 0.474\,\mu$) light.

The radiation from platinum at lower temperatures was studied by fixing the temperature of the platinum strip of the Joly meldometer by means of known melting points in the usual way by placing a minute specimen of the metal or salt on the strip and slowly increasing the heating current until the specimen was observed to melt, when the length of the strip was determined by the electric contact micrometer screw, and the current regulated to maintain this length (and therefore the temperature) constant throughout a series of ob-

[1] Joly, Proc. Roy. Irish Acad., 2, p. 38, 1891.

The Black Body Temperature of Platinum at its Melting Point.

Date, 1904.	No. Lamp Used in H-K Pyr.	Black Body Temp. for Red Light $\lambda = .651\ \mu$.	Date, 1904.	No. Lamp Used in H-K Pyr.	Black Body Temp. for Green Light $\lambda = .550\ \mu$.	Date, 1904.	No. Lamp Used in H-K Pyr.	Black Body Temp. for Blue Light $\lambda = .474\ \mu$.
Apr. 13	No. 156	1,545°C	Apr. 18	No. 156	1,570°C.	Apr. 18	No. 156	1,618°C.
"	"	1,543	"	"	1,585	"	"	1,602
"	"	1,550	"	"	1,578	"	"	1,606
"	"	1,530	"	145	1,577°C.	"	145	1,625°C.
"	"	1,520	"	"	1,577	"	"	1,605
"	"	1,528	"	"	1,561	"	"	1,607
"	"	1,541	"	"	1,577	"	"	1,609
14	"	1,528				"	"	1,621
"	"	1,547	"	132	1,591°C.			
			"	"	1,587			
Mean	"	1,537°C.	"	"	1,576			
Apr. 14	No. 145	1,550°C.	"	"	1,570			
"	"	1,560						
Mean	"	1,555°C.						
Apr. 14	No. 132	1,540°C.						
"	"	1,550						
"	"	1,533						
"	"	1,542						
"	"	1,548						
Mean	"	1,543°C.						
Final Mean		**1,541**°C.	Final Mean		**1,577**°C.	Final Mean		**1,612**°C.
		$\Delta^1 = 239$°C.			$\Delta^1 = 203$°C.			$\Delta^1 = 168$°C.

servations with the optical pyrometer. A second determination of the melting point was always made with the meldometer at the end of every series of observations.

The black body temperatures of polished platinum at 1,500° C., 1,064° C., 782° C. and 723° C., as fixed by the melting points of Pd, Au, NaCl, and KBr, and at 1,315° C. and 1,215° C., as fixed by the observed length of the meldometer strip, are given in the following table:

The results of all the experiments on platinum are best shown graphically in Fig. 7, where for comparison we have added the results obtained by Holborn and Kurlbaum[2] for red light by a somewhat different method.

[1] $\Delta = T - S$, where T = abs. temperature and S = black body temperature.

[2] Holborn and Kurlbaum, Ann. d. Phys., 10, p. 225, 1903.

Radiation from Platinum.

	Red $\lambda = .651\ \mu$			Green $\lambda = .550\ \mu$			Blue $\lambda = .474\ \mu$		
Temp. °C.	Date, 1904.	Lamp Used in H-K Pyr.	Black Body Temp.	Date, 1904.	Lamp Used in H-K Pyr.	Black Body Temp.	Date, 1904.	Lamp Used in H-K Pyr.	Black Body Temp.
	Apr. 12	No. 145	1384°C.	Apr. 18	No. 156	1402°C.	Apr. 18	No. 156	1434°C.
	"	145	1368	"	156	1402	"	156	1423
	"	132	1384	"	145	1410	"	145	1430
	"	132	1370	"	145	1398	"	145	1419
	"	156	1368		Mean =	1403°C.		Mean =	1426°C.
1500°C.	14	145	1378		Δ =	**97**°C.		Δ =	**74**°C.
(MP of Pd)	"	156	1383						
	11	132	1365						
	"	145	1365						
		Mean =	1374°C.						
		Δ =	**126**°C.						
1315°C.	Apr. 15	No. 132	1208°C.	Apr. 15	No. 132	1233°C.	Apr. 15	No. 132	1269°C.
	"	156	1210	"	156	1233	"	156	1244
		Mean =	1209°C.		Mean =	1233°C.		Mean =	1256°C.
		Δ =	**106**°C.		Δ =	**82**°C.		Δ =	**59**°C.
1215°C.	Apr. 15	No. 132	1122°C.	Apr. 15	No. 132	1135°C.			
	"	156	1117	"	156	1138			
		Mean =	1119°C.		Mean =	1136°C.			
		Δ =	**96**°C.		Δ =	**79**°C.			
	Apr. 11	No. 156	969°C.	Apr. 14	No. 132	987°C.			
	"	145	967	"	156	985			
1061°C.	Mar. 23	156	978	"	156	985			
(MP of Au)	Apr. 14	132	978	" 15	156	987			
	"	145	973	"	156	982			
	"	156	980		Mean =	985°C.			
	Mar. 23	with	970		Δ =	**79**°C.			
	"	Wanner	971						
	"	Pyrom.	974						
			972						
		Mean =	973°C.						
		Δ =	**91**°C.						
782°C.	Apr. 11	No. 145	714°C.						
(MP of NaCl)	"	132	720						
		Mean =	717°C.						
		Δ =	**65**°C.						
723°C.	Apr. 11	No. 145	660°C.						
(MP of KBr)	"	132	665						
	"	156	662						
		132	670						
		156	670						
		145	671						
		Mean =	666°C.						
		Δ =	**57**°C.						

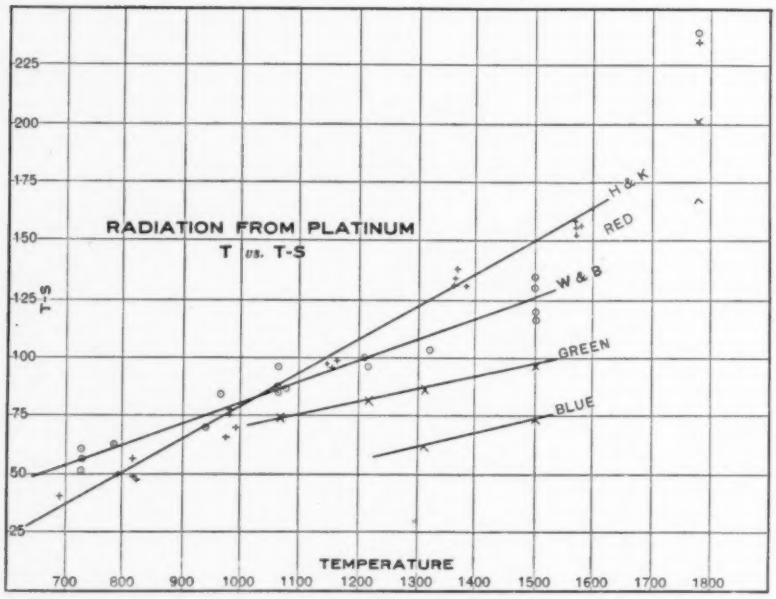


Fig. 7. Radiation from Platinum.

The black-body temperature of the melting point of platinum for red light, as found by these observers, is 1545° C. ($\Delta = 235°$), which is in most satisfactory agreement with the results found by us, which is 1541° ($\Delta = 239°$), obtained by the same method of experiment.

Our results would seem to indicate that the values of Δ increase somewhat less rapidly with rise in temperature than is indicated by the results of Holborn and Kurlbaum. These differences may arise from several causes. The meldometer strip is probably at a slightly higher temperature than indicated by the melting-point calibration, and by an amount which is probably greater at high temperatures. This would tend to make the value of Δ small at high temperatures. In the experiments of Holborn and Kurlbaum the platinum was in the form of a cylinder surrounding a thermo-couple. It is thus possible that the couple was at a slightly higher temperature than the outer radiating surface of the platinum which would tend to increase the values of Δ, especially at high temperatures.

In order to pass through the platinum point ($\Delta = 239°$, red

light) a very sudden bend in the curves is necessary. No evidence is yet at hand to explain whether this can in any way be associated with a decreased radiating power of a substance as it approaches a change of state.

It will also be seen, as has been previously shown, that platinum approaches more nearly to black-body radiation for green and blue than for red light.

Radiation from Other Substances. — Experiments were made on a number of other substances, including clay, copper and iron oxides, and unglazed porcelain to determine the departure of these bodies, at various temperatures, from black-body radiation. Another

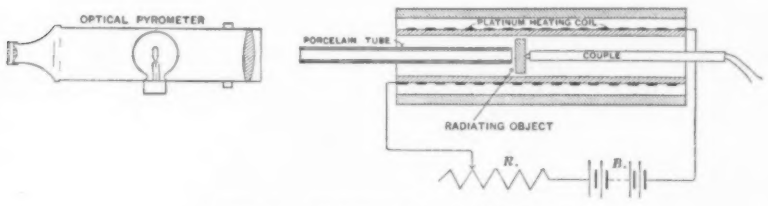


Fig. 8. Radiation Furnace Method.

method of experiment was here necessary, as it is not possible to accurately fix the temperature of oxidizable substances by the meldometer method. The method used will be understood from the following diagrammatic sketch, Fig. 8 :

The radiating substance is placed at the center of an electric furnace. The radiation emitted by the substance under these conditions is a very close approximation to black-body radiation, and its temperature as measured by the optical pyrometer will be the true temperature. As a further check on the optical pyrometer a thermo-couple in contact with the radiating substance was always read. A porcelain tube, open at both ends and blackened on the interior, was then thrust into the furnace and the radiation coming out of this cold tube, which is the radiation of that particular substance, was observed with the optical pyrometer. The temperature measured in this way is the equivalent black-body temperature of the substance for the particular color of light used. The tube was then quickly withdrawn and another measurement taken of the true temperature. There was always a slight cooling due to insertion of

the tube, which was allowed for by taking the observations in the order indicated above. The results of these experiments giving the departure from black-body radiation are given in the following table.

The experiments at the melting point of copper were carried out in a manner similar to those at the melting point of platinum. A copper strip cut narrow at the center was observed with an optical pyrometer at the instant it was fused by an electric current. The temperature of melting was assumed to be 1065° C., corresponding to the melting point of copper in an oxidizing atmosphere, and the corresponding black body temperature was given by the optical pyrometer.

In order to compare the *meldometer method* with the *furnace method* we determined the departure of platinum from black body radiation by both methods. The agreement is even better than we have any right to expect, thus at 950° C., the furnace method gave 74° C., and the meldometer method (by interpolation) 75° C., as the difference between the true temperature and the black body temperature of platinum.

The interesting range of iron and steel in which hardening and annealing operations are carried out is from about 600° C., to 950° C., and as will be seen from the table, the indications of an optical pyrometer in this range, if calibrated in the usual way in terms of black body radiation, will be low by about 20° at the lower temperature and about 40° at the upper temperature.

The radiation from the fine-grained crucible seemed to be at least as black as that from iron, which would hardly be expected. When a fresh piece of thin Russian iron was inserted into the furnace and measurements were immediately taken with an optical pyrometer it was observed that the initial readings were some 20° higher at 1000° C., than when the exidation of the surface was complete, which takes two or three minutes.

Polarized Light from Incandescent Surfaces. — Arago was among the first to observe that the light emitted by incandescent surfaces was partially polarized, the amount of polarized light varying widely for different substances, and increasing with the angle at which the surface was viewed, being *nil* in a direction normal to the surface. Prevostaye and Desain, and Magnus, showed that the infra red

Departure from Black Body Radiation.

Temperature (Cent).	Platinum.	Iron Oxide.	Fine Grain Battersea Crucible.	Copper Oxide.	Unglazed Porcelain.
730°C.					31°, 35, 25, 30 } 30°C.
750°				22°, 28, 25 } 25°C.	
770°		20°, 26 } 23°C.	11°, 16 } 14°C.		
790°		20°, 21, 22, 26, 23 } 23°C.			
950°	76°, 71, 77, 81, 82, 60, 67 } 74°C.				
980°		43°, 43, 46, 53, 45 } 46°C.			
1050°			50°, 58, 57, 52 } 54°C.		
1065°				37°, 50, 33, 37, 43, 43, 30 } 39°C.	

waves are also polarized in the same plane as the light waves. Arago attributed the polarization to refraction, near the surface, of the light coming from molecules below the surface.

Millikan,[1] who has done the most complete work in this field,

[1] Millikan, PHYS. REV., 3, pp. 81, 177, 1895.

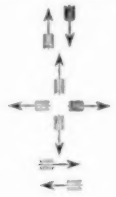
has pointed out that this view of Arago fails to explain why the light coming from platinum near grazing emergence is practically completely polarized, for such light must to a large extent be surface light. His experiments indicate that the polarization is a phenomenon of refraction, and that all the light suffers refraction at the surface. Millikan has examined the amount of polarization in the light emitted by a large number of substances. The phenomenon is most marked in platinum, silver and gold, and is very feeble in the readily oxidizable substances, such as iron and in such substances as glass and porcelain. It is quite marked for iron in the molten state.

Our experiments have been made mainly with a view to determining the amount by which this phenomenon could influence the indications of optical pyrometers that make use of polarizing devices to adjust to equality the light from the incandescent body observed and from the standard comparison light.

In the experiments on platinum the temperature of the horizontal strip of a Joly meldometer, maintained constant by regulating the electric heating current, was measured with a Wanner optical pyrometer, which employs polarizing devices. To eliminate the effect of the sag of the strip the readings were taken with the pyrometer in four positions at right angles. For each temperature the measurements were made at different angles with the normal to the surface. In rotating the pyrometer the portion of the radiating strip viewed was slightly changed, but an examination of the strip showed that the heating was very uniform, the variations not exceeding 4° over a distance of 2 cm. The results of the measurements on platinum are given in the following table:

From the above table it will be seen that if the temperature of a platinum surface is measured with a polarizing pyrometer large errors may result if the effect of polarized light is neglected. Thus, if the surface be viewed at an angle of 50° with the normal, two readings may be obtained differing from one another by 80° C. at 1450 C., *i. e.*, the reading may differ from the actual temperature by 40° or thereabouts.

As the light emitted in a direction perpendicular to surface is not polarized, this source of error can always be avoided by viewing

Angle at Which Incandescent Surface is Viewed.	Position of Slit of Pyrometer with Reference to Incandescent Strip.	Mean Reading Wanner Pyrometer.	Maximum Δ for Two Positions of Slit at Right Angles.
PLATINUM AT 1450° C.			
30°		63	
0		64.6	3.3 divs. = 34°
30		66.3	
50		61.9	
0		66.0	7.6 divs. = 80°
50		69.5	
70		60.8	
0		64.9	8.4 divs. = 90°
70		69.2	
PLATINUM AT 1150° C.			
50°		23.0	
0		24.5	2.8 divs. = 22°
50		25.8	

the surface normally. For most substances on which optical pyrometers are used the amount of polarized light is very feeble compared with platinum, so that its effect is entirely negligible. In some experiments where the incandescent surface of iron was viewed at an angle of 75° the effect was less than 5°. In any case the effect may be eliminated by taking readings in four azimuths, at intervals of ninety degrees.

Effect of Diffuse and Reflected Light. — Diffuse daylight, or light

from other sources which is not reflected directly into an optical pyrometer, will not seriously effect its readings, a rise of only 5° being caused by changing from a dark room to bright daylight.

The magnitude of the effect of directly reflected light is very variable, depending upon the reflecting power of the incandescent body observed, the size and location of the disturbing sources, and difference in temperature between the latter and the observed body.

A platinum strip at 800° C. had its temperature apparently raised 120°, due to direct reflection from a large gas flame, and by 300° when placed within a ring of gas flames.

Iron (oxide), which unlike platinum is a poor reflector at high temperatures, underwent an apparent rise in temperature of 35° for the first case and its temperature could not be observed in the second. At 1100° C., however, turning off and on the ring of flames made no appreciable difference in the reading for iron.

This disturbing effect may be very nearly eliminated by viewing the bright object through a tube which cuts off most of the light from surrounding flames, thus the error of 35° above noted was reduced to 5° by this means.

The Measurement of Very High Temperatures. — The temperatures that have been discussed thus far are within the range controlled by thermo-couples calibrated to agree with the gas scale to about 1150° C., which marks at present the upper limit of satisfactory gas thermometry. The thermo-couple scale is then extrapolated for 500° or 600° more.

Already there are many operations, such as those carried out in the Moissan furnace, the Goldschmidt thermite process, the production of carbides and metallurgical products in electric furnaces, and many pyrochemical reactions, that involve temperatures of 2000° or over. It therefore becomes necessary to establish at least some tentative scale that can be used at these extreme temperatures.

Attempts are being made by Nernst and others to estimate these high temperatures by means of chemical phenomena taking place at high temperatures, but this work is still in a preliminary state. For this purpose, therefore, recourse must be had alone to the extrapolation of the laws of radiation which have been verified throughout the range of measurable temperatures.

Lummer and Pringsheim [1] have recently taken a single set of observations on an electrically heated carbon tube in an atmosphere of nitrogen, using three radiation methods: photometric (Wien's law), spectrophotometric ($\lambda_m T = A$), and total radiation (Stefan-Boltzman law), the results agreeing to 20° at 2300° C. absolute.

From our own work it would seem that the radiation laws are still in agreement at the temperature of the arc.[2] Our measurements have given as the black body temperature of the hottest part of the positive crater 3690°, 3680° and 3720° absolute, as determined with the Holborn-Kurlbaum, Wanner, and Le Chatelier pyrometers, based on the extrapolation of Wien's law. Féry [3] gets for this temperature 3760° by a method based on Stefan's law.

On the basis of these experiments it would seem that the several laws of radiation are in quite satisfactory agreement at the highest attainable temperatures, and thus serve to define the same scale of temperatures.

[1] Lummer and Pringsheim, Verh. d. Deutsch. Phys. Ges. (5), 1, p. 3, 1903.

[2] Waidner and Burgess, PHYS. REV., 19, p. 241, 1904; Bulletin, Bureau of Standards, 1, p. 109, 1904.

[3] Féry, C. R., 134, p. 977, 1902.

A LIMITATION IN THE USE OF THE WANNER PYROMETER.

BY LEON W. HARTMAN.

THE accurate determination of the temperature of a body heated to a state of incandescence presents many vexatious difficulties to the scientific investigator. As yet the most satisfactory as well as the most accurate method of measuring high temperatures is based on the thermo-electric principle, in which the electromotive force generated by a thermo-element, raised to the temperature of the source in question, is measured. This measurement having been made, the required temperature can at once be read from the calibration curve of the thermo-element. This method, however, has its limitations and objections. It is often inconvenient or impossible to introduce a thermo-element into the heat source whose temperature is sought; suitable sensitive apparatus in portable form may be wanting; and in all cases one is limited to temperatures lower than the melting point of the thermo-element. To avoid these difficulties, therefore, pyrometers of another sort, depending upon various principles, have been designed. Among the latter are those depending upon optical and photometric principles. Two forms which have been elsewhere described may be mentioned as illustrations, *viz.*, the optical pyrometer of Holborn and Kurlbaum [1] and the Wanner pyrometer. [2]

As illustrating the optical principle involved in the Kurlbaum instrument, one may place in front of an incandescent body whose temperature can be arbitrarily increased or decreased, a second incandescent body, for example the filament of a glow lamp, whose temperature under given conditions is sought. If with the naked eye or by means of a telescope one views the filament, in general, one body will appear brighter than the other. When the two

[1] Ann. der Physik, 10, 225, 1903.

[2] Ann. der Physik, 2, 141, 1900; Phys. Zeitschr., 1, 226, 1900; 3, 112, 1901.

bodies are equally bright, both have the same temperature and the lamp filament will apparently vanish, leaving the first source only as a background. This condition can be most simply brought about by varying the temperature of the filament until the desired point is reached. If the source serving as a background is the interior of a platinum oven whose temperature can be measured by means of a thermo-element, the temperature of the filament of the glow lamp can be determined for varying current density, and this in turn will serve as a sensitive and portable form of pyrometer. Naturally the two sources should emit light of the same color; otherwise, light of a definite wave-length should be used. In the Wanner instrument, which is in reality a photometer with polarizing Nicols, light from a glow lamp mounted beneath the apparatus, and burning under fixed conditions, is compared with the light from the source whose temperature is desired. When the intensity of the field due to the glow lamp is seen to be equal to the intensity of the field produced by the other source, the position of the analyzer is read off from a graduated circular scale, and from a prepared table given out with the instrument the corresponding temperature can be taken. Simplicity of form and construction, and accuracy and rapidity in making temperature readings, are the advantages claimed for this instrument.

Recently in making a series of measurements to determine the temperatures of a number of different-sized platinum wires, when the temperatures varied from 700° C. to 1500° C., it was the writer's privilege to use a Wanner pyrometer. From the values obtained it was suspected that the instrument gave temperature readings much below the true values. To test the matter, a platinum oven containing a piece of magnesium oxide enclosing the end of a thermo-element was mounted on a stand in front of the telescope of the pyrometer. It was found that the temperatures of the heated oven as recorded by the pyrometer and by the thermo-element were in good accord. The platinum wires mentioned above were then mounted in front of the oven and the principle of the Kurlbaum pyrometer, as described heretofore, was utilized in determining the actual temperatures of the incandescent wires. The latter, seen against the background of incandescent magnesium oxide within

the oven, were observed through a telescope and the current flowing in the wires was gradually varied until they apparently vanished from the field of view. The platinum wires and the furnace were then at the same temperature. The temperatures of the oven and wires, and the temperatures of the wires alone, were then measured by the pyrometer, and a marked difference between the two series of readings was found to exist. Then a whole series of measurements was made with the platinum wires placed in front of the oven. In all four different platinum wires were thus tested. In Fig. 1 the

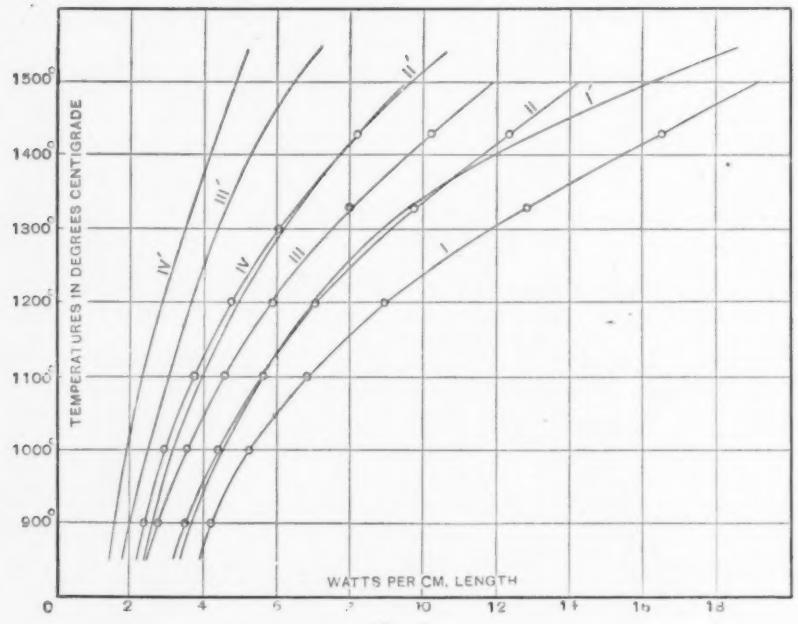


Fig. 1.

curves expressing the relation between temperature and watts per cm. length are drawn. The deviation of the one series of observations from the other is thus graphically shown. Each curve in this figure is the mean of three other curves, each of which was made at a different time. The curves obtained from the observations made with the pyrometer and wires alone, are designated I., II., III. and IV.; the primed curves, obtained by placing the wires in front of the oven, as above described, are designated I′., II′., III′. and IV′. The power consumed was obtained in the usual way from the

measurements of the current strength and potential difference between the terminals of the wires. The instruments used throughout had been carefully calibrated so that no error from this source is present.

Under the two different conditions stated in the preceding paragraphs the values of the Watts per cm. length, required to give temperature readings on the pyrometer equal to those designated below, were determined. These values, together with the diameters of the wires, are recorded in the following table. The primed and unprimed letters have the same signification here as above.

Wire.	Diameter.	Temperatures in Degrees Centigrade.						
		900°	1000°	1100°	1200°	1300°	1400°	1500°
		Watts per cm. Length for Above Temperatures.						
I	0.0690 cm.	4.20	5.60	6.52	8.95	11.85	15.44	19.13
II	0.0440 "	3.50	4.40	5.65	7.07	9.11	12.58	14.24
III	0.0300 "	2.75	3.55	4.55	5.83	7.50	9.60	11.91
IV	0.0194 "	2.40	2.95	3.75	4.75	6.05	7.70	9.50
I′	0.0690 "	3.67	4.57	5.61	7.12	8.85	11.38	16.33
II′	0.0440 "	2.60	3.14	3.98	4.98	6.16	6.90	7.68
III′	0.0300 "	2.18	2.43	3.03	3.70	4.38	5.28	6.47
IV′	0.0194 "	1.55	1.90	2.30	2.87	3.50	4.14	4.88

From a mere inspection of this table it will be seen that the percentage error in the energy measurement was the greatest in the case of the smallest wire; and that this error varies with increasing temperature from 20 per cent. to 100 per cent. The probable cause of this error is a diffraction effect produced when one has a source of illumination with such small dimensions. In any case this instrument is to be used with caution in measuring the temperatures of small narrow sources such as incandescent rods or wires. For incandescent bodies presenting considerable surface such as the interior of furnaces or pottery ovens, the instrument seems to satisfy the claims made for it.

For the apparatus furnished, for the many courtesies shown, and for the helpful suggestions given I wish, in conclusion, to acknowledge my indebtedness to Prof. W. Nernst, in whose laboratory the above work was performed during a more extended investigation.

GÖTTINGEN, May 1, 1904.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

SPECTROPHOTOMETRIC STUDY OF SOLUTIONS OF COPPER AND COBALT.[1]

BY B. E. MOORE.

THE effect of dissociation upon the color of solutions may be studied in two ways — by the photographic or by the spectrophotometric method. The latter has the advantage of quantitative determination of absorption both in strong and in dilute solution. The latter method has been used by a number of observers, who have generally confirmed Ostwald's law, viz: "That the color of dilute solutions having a common ion is identical."

The method consists in the study of the absorption, of such solutions in the concentrated and dilute form. It occurred to the writer that these solutions could be diluted in another uncolored solution containing a common ion of great concentration, and thus prevent a large part of the dissociation, or, what is the same thing, repress the dissociation by the principle of mixed electrolytes.

The present experiments are limited to the study of the sulfate, chloride, nitrate and acetate of copper; and the sulfate, chloride and nitrate of cobalt. They have been given the usual treatment and have besides been diluted in strong acids corresponding to the negative ion of the salts. The method eliminates the absorption of all components except the one which is studied.[2]

All the copper salts, in dilute water solutions have identical absorption per equivalent in the strong absorption region at the red end of the spectrum. The cobalt salts also give identical absorption in dilute water solutions in the green band. In the more transparent regions, blue and red, the indications are that the cobalts might be identical in

[1] Abstract of a paper presented at the St. Louis meeting of the Physical Society held on September 16, 1904.

[2] PHYSICAL REVIEW, Vol. XII., p. 151.

great dilution. They are, however, far from it at the dilutions studied. In the regions nominally transparent, the copper salts show great divergence in the dilute water solutions, and the indications are for larger divergence with greater dilution. The standard solution of copper sulfate and this solution diluted both in water and acid give identical absorption per equivalent in the red band, *i. e.*, in this region the color of the ion and molecule are identical. In this same region the nitrate and chloride become relatively more transparent upon dilution.[1] When diluted in acid they become relatively darker and, if the acid is of adequate strength, even become darker than the original solutions. The acetate shows identical absorption in all solutions, and in the red region the absorption is more than twice that of the sulfate. The three cobalts become relatively more transparent upon dilution. Treating then with acids darkens the dilute solutions of the chlorides and nitrates but makes the sulfate more transparent. Possibly some of the cobalt sulfate was precipitated by the sulfuric acid treatment.

[1] Müller in Drude Ann., XII., p. 767, states there is an increased absorption of the copper nitrates and acetates upon dilution.

NEW BOOKS.

Thermodynamics and Chemistry; a non-mathematical Treatise for Chemists and Students of Chemistry. By P. DUHEM. Authorized translation by GEORGE K. BURGESS. New York, John Wiley & Sons, 1903. Pp. xxi + 445.

This book presents the main facts of physical chemistry in a very clear way without the use of elaborate mathematical methods which would only bewilder those for whom the book is intended. The various theorems, which stand out prominently in italics, are stated very concisely after a short preliminary discussion in each case, and, nearly every theorem is illustrated by one or more suitable examples chosen from the research literature of physical chemistry, references being given.

These illustrative examples, in consideration of the great number of them, constitute the most valuable feature of the book. It is perhaps the best treatise on physical chemistry at present available for chemists and for students of chemistry. The author and his translator have done a good service and they deserve much credit.

The ideas of work and energy, of heat and internal energy, of chemical calorimetry, of thermal equilibrium and reversible transformations, and the fundamental principles of chemical equilibrium from the point of view of thermodynamics are briefly developed in the first five chapters. Chapters VI. and VII. are devoted to the phase rule in general, introducing the ideas of monovariance and multivariance of systems, and these ideas are developed in detail in Chapters VIII., IX., X., XI., XII., XIII., XIV. and XV. The chemical mechanics of perfect gases is discussed in Chapter XVI, capillary actions in Chapter XVII., false equilibria in Chapters XVIII. and XIX., and explosions in Chapter XX.

The first five chapters are not so satisfactory as the remainder of the book. The old notion of the mechanical equivalent of heat is retained by the author. No quantitative notion of heat can be more satisfactory or more simple than that which is based directly upon the equivalence of heat and work, and it is time that every one should speak of the specific heat of water rather than of the mechanical equivalent of heat. Also we do not believe that the author has reduced to its simplest and most precise terms the thermodynamics which he gives in Chapter V. Thermodynamics presents at the present time a great many theorems which are developed in many of our present day manuals in ways which

never could lead to anything but error or to previously known conclusions and the severe limitations which Professor Duhem has chosen to place upon this book do not wholly clear him of this criticism, in our opinion.

Mr. Burgess' work is on the whole well done inasmuch as it seems to be faithfully accurate and it is intelligible, although in some places slightly awkward, partly because of the numerous French idioms which have been retained and partly because of apparent carelessness of expression; although the evidences of carelessness are not many. To justify this criticism, which we hesitate to make in view of Mr. Burgess' service to English-speaking students, we give one of the very few evidences: "According to the law of the displacement of equilibrium by the variation of temperature, the mass of hydrogen sulphide gas formed within a system where hydrogen and sulphur are heated at constant volume should be, at the instant of equilibrium, the feebler as the temperature were the higher."

In conclusion we are pleased to state that the reading of the book has been on the whole very pleasant and very profitable to us.

W. S. FRANKLIN.

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